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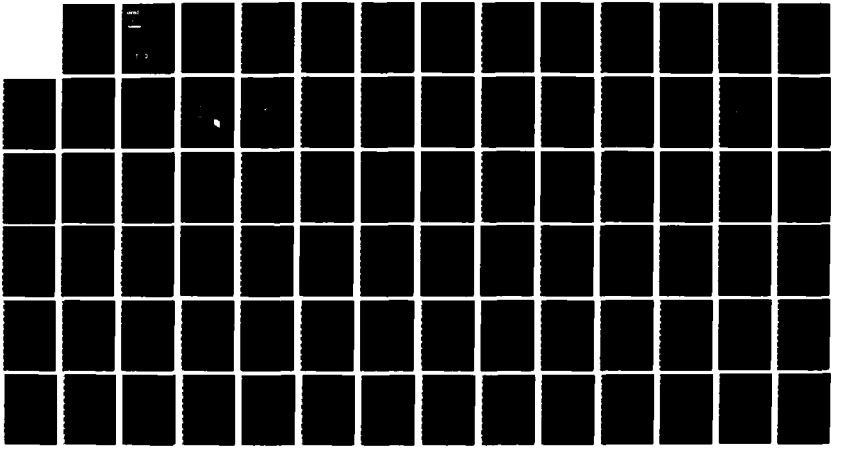

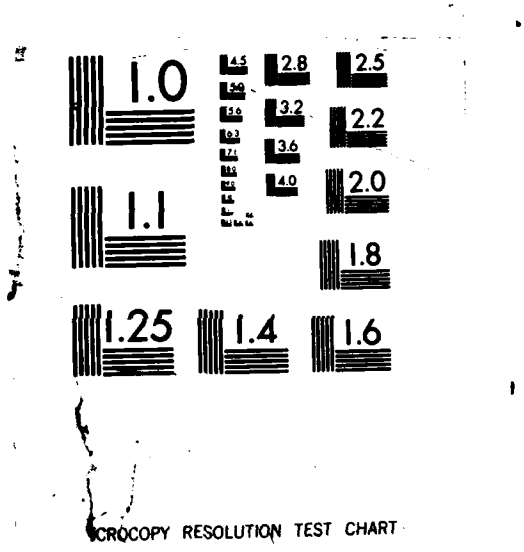
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MARTIN MARIETTA

Application of Solid Sorbent Collection Techniques and High Performance Liquid Chromatography with Electrochemical Detection to the Analysis of Explosives in Water Samples

Final Report

M. P. Maskarinec
D. L. Manning
R. W. Harvey

Supported by

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground, MD 21010-5401

Project Officer: Mary Ann Ryan

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Methods were developed for the determination of several explosives components (nitro-organic compounds) in environmental waters. The methods are based on Porapak resin adsorption and Amberlite XAD-4 resin adsorption of the explosives components from aqueous samples. Following desorption with acetone, the explosives are measured by high performance liquid chromatography with electrochemical detection. The technique provides a high degree of selectivity and sensitivity for these compounds in actual samples. Detection limits approach 1 µg/ℓ for many components.

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APPLICATION OF SOLID SORBENT COLLECTION TECHNIQUES AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION TO THE ANALYSIS OF EXPLOSIVES IN WATER SAMPLES

M. P. Maskarinec, D. L. Manning, and R. W. Harvey

Analytical Chemistry Division
Oak Ridge National Laboratory

FINAL REPORT

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EXECUTIVE SUMMARY

The objective of this program was to validate analytical methodology based on solid sorbent techniques for the isolation, and quantitative analysis of munitions components in water. Previous laboratory work had identified candidate methodologies for 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), nitroglycerin (NG), pentaerithritol tetranitrate (PETN), and N-methyl-N,2,4,6-tetranitroaniline (TETRYL). In this study, these seven components were targeted, and HMX and nitroguanidine were added later. HMX was added because it is often a byproduct of RDX production and is found in water at munitions plants. Nitroguanidine was added because available methods were inadequate. Three resins were selected based on the preliminary laboratory study for evaluation across the eight components. These resins were Porapak-R, Porapak-S, and XAD-4. The resins were evaluated initially for background contamination, flow rate at constant pressure, and adsorption/desorption characteristics. XAD-4 had the lowest resistance to flow, followed by Porapak-S and Porapak-R. Porapak-S appeared to be the cleanest of the three resins although all contained some interfering contaminants.

All compounds except nitroguanidine were recovered adequately. TETRYL was best recovered using XAD-4. Nitroguanidine was not recovered using any resin. A physical concentration process (rotary evaporation) was found most suitable for nitroguanidine. Precision of the analysis was assessed by performing all measurements in triplicate. Accuracy was assessed in two ways: comparison of the resin adsorption with solvent partition, and by comparison with direct analysis on the aqueous samples where possible. Analysis was by high performance liquid chromatography with reductive electrochemical detection. Detection limits were less than 4 ug/L for all compounds, and the detector was much less sensitive to the interferences which complicated UV detection at 254 and 210 nm.

The definitive test of any analytical method is in its application to real samples. To assess the validity of this methodology, samples were collected at Volunteer Army Ammunition Plant (VAAP), Milan Army Ammunition Plant (MAAP), Sunflower Army Ammunition Plant (SAAP), and Holston Army Ammunition Plant (HAAP). The trip to VAAP was primarily for the purpose of evaluating sample throughput and experimental design. On-site quantitative analyses were performed at both MAAP and HAAP, while samples were also sorbed and transported to ORNL for desorption and comparative analysis. The results showed good agreement between the resin desorption method and both direct analysis and solvent partition for all components (except TETRYL).

The range of real sample concentrations was from < 1 ug/L to > 30 mg/L total explosives. Even at the highest level, little breakthrough on the resins was observed. Indirect evidence from the samples at HAAP indicated that both acetylated HMX (SEX) and acetylated RDX (TAX) could be effectively sorbed as well.

Sufficient data has been generated to conclude that the analytical protocol is capable of producing reliable results for RDX, TNT, 2,6-DNT, TETRYL, and 2,4-DNT in the range 1 ug/L to 10 mg/L. HMX can also be analyzed reliably if no SEX and TAX are present.

Although not found in any samples, NG and PETN were isolated and recovered for fortified water samples using the methodology described here. Detection limits were <3 ug/L for these compounds. This represents a substantial improvement over existing methods for nitroaliphatics and is perhaps the first method capable of detecting these components in groundwater.

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INTRODUCTION

Nitrated organic compounds are the most widely used munitions components. These compounds have been and continue to be produced in large quantities, and are therefore, subject to regulation by environmental agencies. The main concern, from an environmental standpoint is contamination of aquifers. Both surface water and groundwater, in and near facilities producing, handling, and storing munitions has the potential for contamination by these compounds. While various toxicology (1-5) studies have been carried out on these compounds, there exists no definitive toxicology data base for the establishment of acceptable levels of aquifer contamination. Furthermore, reliable analytical methodology for the determination of these components in aqueous samples is lacking.

The chemical structures of a variety of munitions components are shown in Figure 1. Three general classes of compounds are normally encountered: nitramines, nitrotoluenes and nitroaliphatics (nitrate esters). The inherent differences in chemical structure lead, of course, to significant differences in chemical properties. For example, the nitrotoluenes have in general greater water solubility than the nitramines. However, the nitramines have much lower solubility in organic solvents than the nitrotoluenes. The octanol/water partition coefficient is therefore higher for the nitrotoluenes than the nitramines. These anomalies make the choice of an extraction solvent or sorbent less than straightforward. Furthermore, these compounds have a wide range of chemical stabilities in aqueous systems. The nitrate esters are reported to decompose rapidly (6) while the nitrotoluenes are quite stable. This complicates matters of sample collection and storage.

Since the first description of the use of resin columns in water extraction (7), these systems have received much attention. For the purposes of the present work, these systems appear to have several advantages over solvent partition systems. First, resins should be available which exhibit specific sorptivity toward nitro groups, allowing the use of one isolation technology for all compounds of interest. Second, the resin sorption can be done in the field immediately after sampling, avoiding liquid phase preservation problems associated with adsorption on container walls, photolysis, and biodegradation. Third, the sorption of these compounds on resins would be expected to reduce the costs associated with sample shipment. Preliminary investigations indicated that three resins, Amberlite XAD-4, Porapak-R, and Porapak-S, would meet the above criteria (8). Using these resins as a starting point, this work attempted to identify the limitations and strengths of resin methods for munitions components, and to select an optimum resin method for field use.

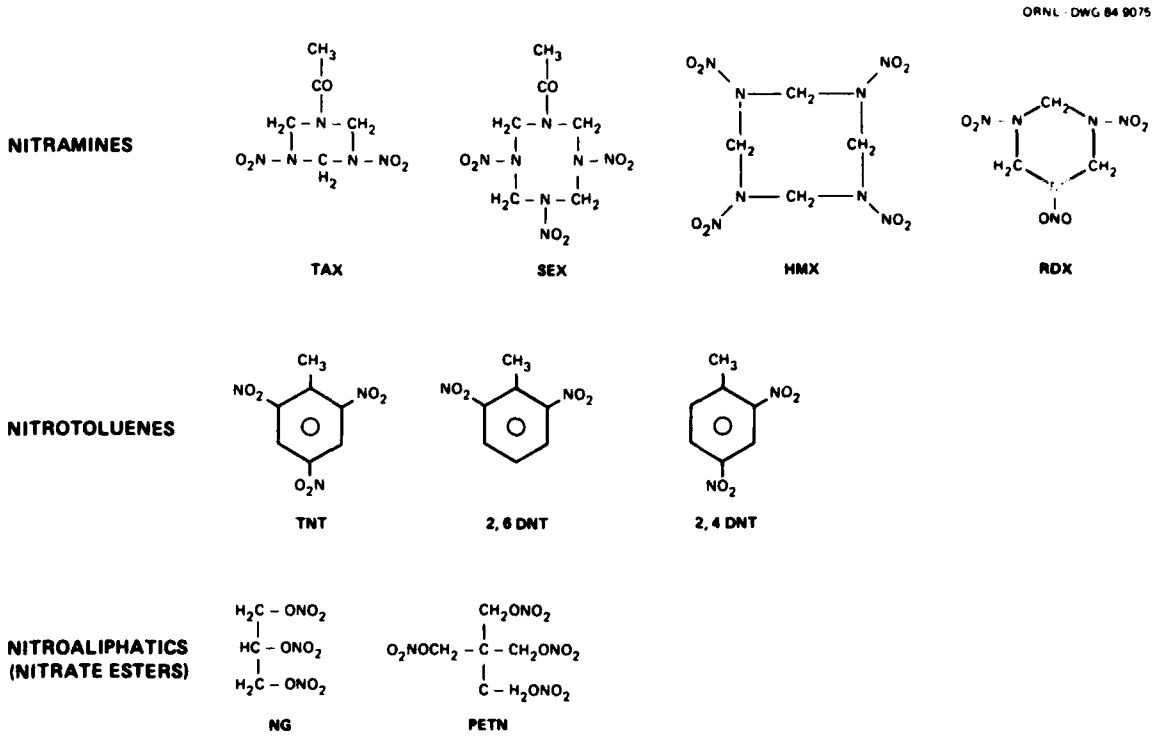

Figure 1. Structures of Explosive Compounds

For the purpose of this work, the following compounds were chosen: HMX, RDX, TNT, 2,6-DNT, 2,4-DNT, NG, PETN, and TETRYL. Nitroguanidine was added at a later date. These were selected based on earlier analytical successes (8), and also on expectations of occurrence in groundwater. These also represent a wide range of chemical properties. While earlier work had been focused on the applicability of resin techniques to individual compounds in pure water, it was our hope that a single resin technique could be used which would allow the isolation of the munitions components as a class from groundwater, followed by multicomponent analysis. This would have the advantages of: 1) a single sample could be used to "screen" for the presence of contamination; 2) byproducts and degradation products might also be collected; and 3) a single analytical protocol could be used regardless of the expected composition of the sample. In order to achieve this objective, it was necessary to devise a resin-based system with selective adsorptivity toward nitro groups, and to develop an analytical technique capable of the elution, separation, and detection of these compounds.

As mentioned earlier, the previous work (8) had identified XAD-4, Porapak-S, and Porapak-R as candidates for adsorption of the general classes of explosives components. The authors reported the unusual finding of the Porapaks outperforming the more widely used XAD-4. A closer look at that data indicates that the XAD-4 performed as expected--as a nonspecific reverse-phase adsorbent. The Porapak resins, on the other hand, appeared to more selectively adsorb nitroorganic compounds. These findings are complicated by several facts: 1) different particle sizes were used for different resins; 2) no "real" samples were analyzed; and 3) the explosives components were tested singly--thus, eliminating any possible interactions which could influence adsorptive behavior. Nevertheless, that work provided a valuable starting point for the evaluation of solid sorbents as isolation media for explosives in environmental waters.

Both gas chromatography (GC) and high-performance liquid chromatographic (HPLC) methods have been applied to the analysis of nitrated munitions components. A variety of gas chromatographic detectors, including the nitrogen-phosphorous detector (9), electron capture detector (10), thermionic ionization detector (11), and thermal energy analyzer (12) detect these species with good to excellent sensitivity and selectivity. However, these thermally-labile species are subjected to a significant amount of heating during any gas chromatographic analysis, thereby introducing the likelihood of partial and irreproducible degradation. Gas chromatographic analysis of many of these compounds, consequently, would be suspect at best.

Liquid chromatographic methods, by contrast, never volatilize the sample; hence, thermal degradation is not a complication. Nitrated munitions components may be detected using the following four

approaches: (a) UV absorption (13,14); (b) chemical reduction to the corresponding amine followed by fluorescence detection (15-17); (c) photolytic cleavage of the C-NO2 bond to form nitrite ions which are later electrochemically oxidized to nitrate (18); and (d) electrochemical reduction of the nitro group to the corresponding amine (19). Both spectroscopic approaches would be appropriate for aromatic explosives, but comparatively very new insensitive for saturated species such as NG and PETN. The wide range of response makes this approach less than practical. The LCEC determination of munitions components has been investigated by Bratin, et al. (19). These workers elucidated the reduction mechanism for nitrated compounds, and established detection limits of approximately 0.1-0.4 ng per explosive tested. Similar calculations for a variety of explosives using the UV detector (200 nm) yielded a detection limit of 1-160 ng per explosive. Thus, LCEC possesses the sensitivity required to detect trace concentrations of munitions components in aqueous samples. Furthermore, the detector response will be primarily affected by the number of nitro groups per molecule. This approach could then be applied to the determination of by-products and degradation products of the compounds of interest, and yet still be selective.

The overall objective of this work was to develop a resin adsorption system suitable for the isolation of nitro compounds from water, and to utilize high performance liquid chromatography with reductive electrochemical detection (HPLC/EC) to achieve detection limits of 1 ug/L.

EXPERIMENTAL

Sample Collection and Handling

Variables such as mesh size of resin cartridge design and pumping rate were kept consistent with earlier work (8). All water samples were collected in 3.8 L amber flint glass bottles. Sufficient sample was collected (6 L) to allow for triplicate analysis by solvent partition and adsorption on each of three resin sytems. Well water samples were collected using a Teflon bailer (Cole-Parmer, Chicago, IL). Surface water samples were collected using a grab sampler (Bel-Art, Pequannok, NJ). After collection, the samples to be analyzed using solvent partition were divided into three 500 mL aliquots (clear flint glass bottles) and stored in the dark at 4°C until extraction. Samples for resin adsorption were passed through the resin columns immediately after returning to the laboratory.

For solvent extraction, 500 mL of sample was extracted three times with 50 mL of methylene chloride. The methylene chloride was taken to near dryness with flowing N_2. Eight mL of acetone and 0.5 mL H_2O

was added, then taken to near dryness with N_2, and diluted with HPLC mobile phase to a final volume of 2 mL. The sample was filtered through a 0.45 um Millipore filter into a 1 dram vial. For resin adsorption, the resin was prewashed with acetone by Soxhlet extraction for two or more hours. After drying in a vacuum oven at 30°C for one or more hours the resin cartridges wre prepared as follows:

Five mL graduated disposable pipets were packed with approximately 1.1 grams (3 mL) of the sorbent and retained with plugs of glass wool. After packing, the sorbent was further cleaned by pumping about 200 mL of acetone through each pipet. The columns were then conditioned by pumping 100 mL of distilled water through them. One mL of H_2O was left on the columns. The ends of the columns were sealed with Supelco plastic column caps until use.

On-site sampling with the sorbent cartridges was carried out as follows: Sampling was accomplished by pumping (LAB PUMP, FMI, Oyster Bay, NY) 500 mL of sample through a conditioned sorbent column at 10-15 mL/min. The column was then rinsed with 5 mL of distilled water. The loaded sorbent column was left with one mL of distilled H_2O, and sealed for transport back to the laboratory. The loaded columns were purged of excess water for several minutes with a stream of N_2. The sample was stripped from the loaded sorbent column with 10 mL of acetone by gravity flow. The 10 mL of acetone was evaporated to <2 mL under a stream of N_2. The final volume was adjusted to 20 mL with mobile phase and filtered through a 0.45 um filter (Rainin Co., Nylon 66) prior to injection onto the HPLC column.

Preparation of Mobile Phase

Reagents:

0.025 M Sodium acetate, pH 6. Dissolve 4.1 g sodium acetate in 500 mL distilled water, adjust to pH 6 with acetic acid. Dilute to 2 L with distilled water.

1-Propanol, Distilled in glass, Burdick & Jackson
Mobile Phase: 1-Propanol, 0.025 M sodium acetate (pH 6) 30/70 v/v). Add 300 mL 1-propanol to 1 L volumetric flask. Dilute to mark with 0.025 M NaAc solution. Filter through 0.45 um Nylon-66 filter. Add to the 2 L flask for pump A. For 20/80 (v/v), add 200 mL 1-propanol to 1 L volumetric flask. Dilute to the mark with 0.025 M acetate solution. Filter through 0.45 um Nylon-66 filter. Add to 2 L flask for pump B.

Apparatus:

Electrochemical detectors used in this work were a Bioanalytical Systems (BAS) Model LC4B(17-D) dual electrode detector and an EG&G Princeton Applied Research (PAR) Model 310 polarographic detector and Model 174A controller.

The BAS detector, which is the electrochemical cell illustrated in Figure 2 is a BAS TL-6A thin layer cell assembly which consists of a single gold-mercury working electrode, glassy carbon counter electrode and an RE-1 Ag/AgCl reference electrode. The reference electrode is housed down stream in an RC-2A reference electrode compartment. The LC column was a 25 x 0.46 cm C18 (5 um particle size) Dupont Zorbax column. The injection valve was a Rheodyne Model 7120 fitted with a 20 uL loop and mounted vertically for sample degassing similar to the method proposed by Lloyd (21). A Hewlett-Packard Model 7045A X-Y recorder and a Hewlett Packard Model 3390A reporting integrator were used for data collection.

The thin layer mercury thin film electrodes were prepared following the recommendations of Bratin, et al (19,20). Enough triply distilled mercury was placed on the highly polished gold electrode to cover the entire surface. After approximately 3 minutes, the excess mercury was removed with a straight edge. At this point, the electrode was viewed edge-on with a hand magnifying glass. If a "bulge" was noticable, the straight edge was passed across the electrode again to remove more mercury. (Keep the mercury film as thin as possible, consistent with complete coverage of the gold surface.) The importance of achieving good amalgam formation cannot be overemphasized. Usually a new amalgam surface could be applied over an old amalgam several times before the old amalgam surface had to be removed with 6 M nitric acid and the electrode repolished. The old amalgam was wiped with a tissue to remove any excess mercury film. The amalgam surface was renewed in the same way as with a new electrode. (Detailed instructions for electrode maintenance are furnished with electrodes and polishing kits from Bioanalytical Systems, Inc.) The PAR detector was used in the hanging mercury mode. A medium size hanging mercury drop electrode (HMDE) was used throughout.

A Perkin-Elmer Series 2 liquid chromatograph was fitted with the essential dissolved solvent oxygen removal apparatus for both pumps (19,20) as illustrated in Figure 3. The mobile phase vessel is a two liter three neck flask fitted with a condenser, thermometer and lines for mobile phase delivery and gas sparging. The gas sparging line from the cylinder to the mobile phase vessel is 1/8 in. OD copper tubing fitted with a Nupro Fine metering needle valve for flow regulation. The sparging line to the injection valve is 1/16 in. OD stainless steel also fitted with a Nupro Fine metering needle valve. The connections to the nitrogen saturation vials (3.5 mL screw cap)

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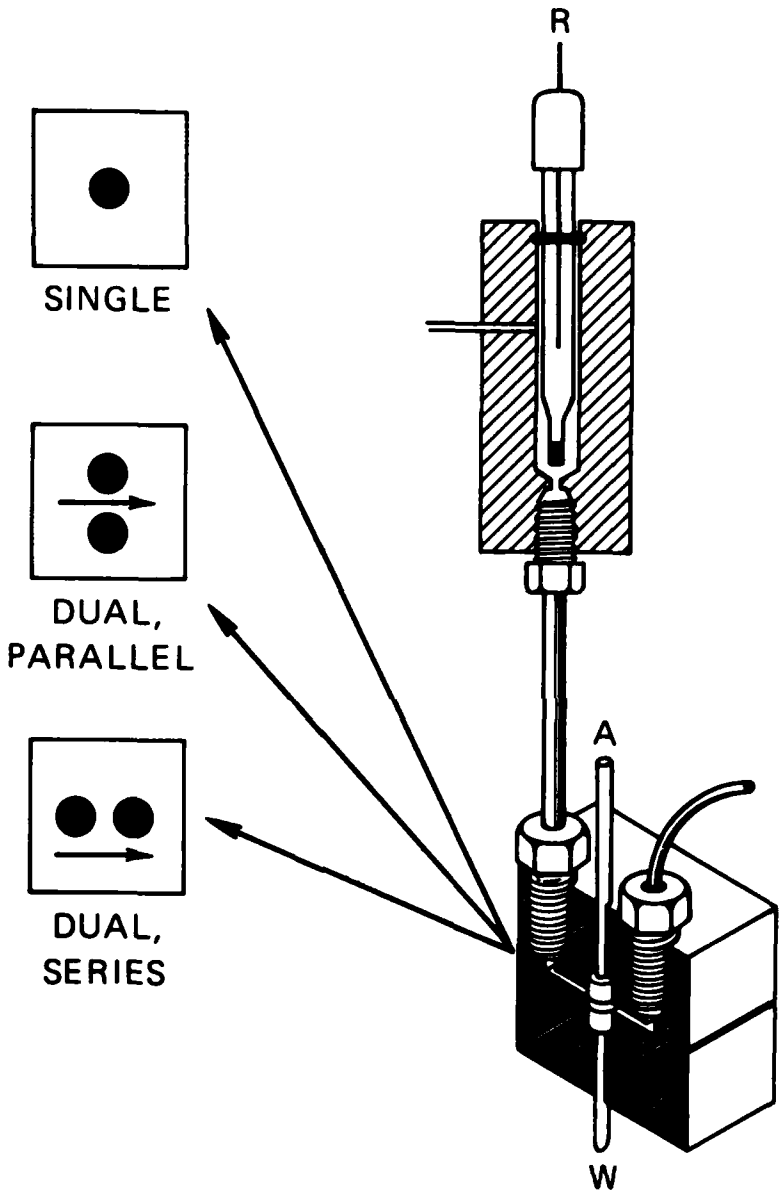

Figure 2. Electrochemical Detector

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BLOCK DIAGRAM FOR REDUCTIVE ELECTROCHEMICAL DETECTION

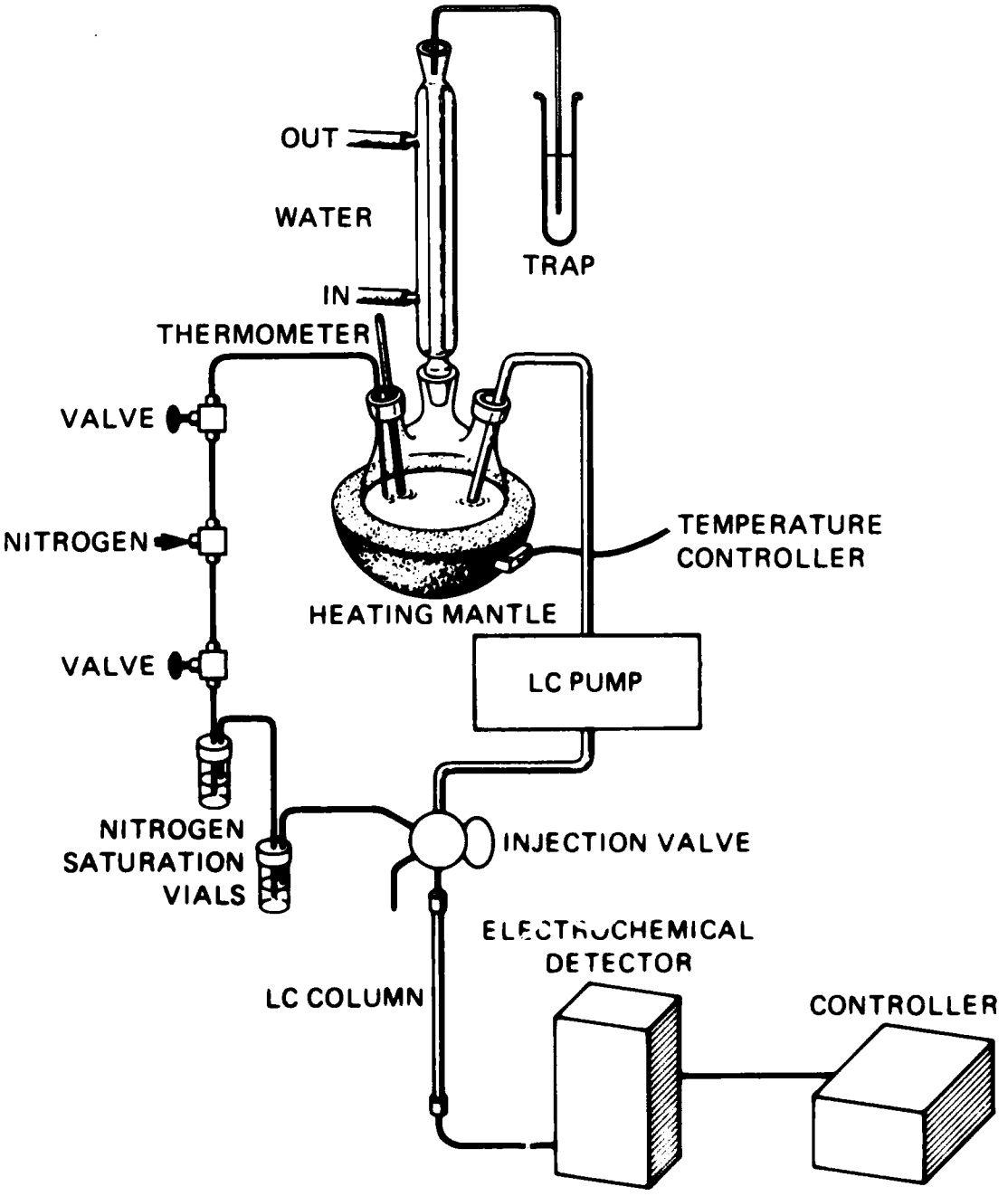

Figure 3. Block Diagram for Reductive Electrochemical Detection

are through 12 mm Teflon-coated silicone discs. The mobile phase delivery line from the reservoir to the pump inlet is 1/8 in. OD stainless steel. From the pump outlet to the electrochemical detector, all lines are 1/16 in. OD stainless steel. A BAS Model MF 4000 flow through pulse damper was installed between the pump outlet and injection valve. The lines for mobile phase delivery and gas sparging are attached to the reservoir through gas tight rubber stoppers and extend about 2 inches inside the flask. Teflon lines (1/8 in.) are fitted to the metal tubing and extend into the mobile phase. The ends of the Teflon lines immersed in the mobile phase are fitted with stainless steel solvent inlet filters, 1/2 in. diam. x 1 in. long, 5 um pore size. The gas flow through the SS filter for sparging is a steady stream of small "micro" bubbles.

Procedure

Deoxygenation of Mobile Phase: Place 2 L of filtered mobile phase into the 2 L flask shown in Figure 3. The system is made air tight by the stainless lines, thermometer and trap connections passing through tight fitting rubber stoppers. The trap at the top of the condenser is terminated in about 5 cm water which allows for a slight overpressure of inert gas inside the system. With inert gas (nitrogen or helium) slowly sparging through the mobile phase (ca. 2-4 mL/min) adjust variac or temperature controller to heat mobile phase to 60°C. Maintain these conditions for at least 24 hours. Lower temperature of mobile phase to ca. 30°C and maintain inert gas sparging at ca. 1 to 2 mL/min. An alternate and effective method of degassing the mobile phase is by purging with helium at 120 mL/min for 30 min, and then continuous sparging at 2-4 ml/min.

Deoxygenation of Sample: With the vertically mounted injection valve which is illustrated in Figure 4 in the inject position, insert the 1 mL syringe without plunger in the needle port and turn valve to load position. Start inert gas flow as evidenced by bubbling through the gas saturator vials and at this point mobile phase from the loop and excess sample solution from the previous injection will back-up into the syringe. Remove this solution with a disposable pipet. Add 200 uL ethanol and allow gas to bubble through for about 10 secs to rinse syringe. Remove ethanol with disposable pipet. Place ca. 100-200 uL sample in syringe and degas it at ca. 1 bubble/sec for about 3 mins. Insert plunger just at top of syringe then turn off gas. Push in plunger to fill loop with sample, turn valve to inject, then remove and rinse syringe.

Controller Operation: Read and be thoroughly familiar with the operations manual for the controller before operation. The operation

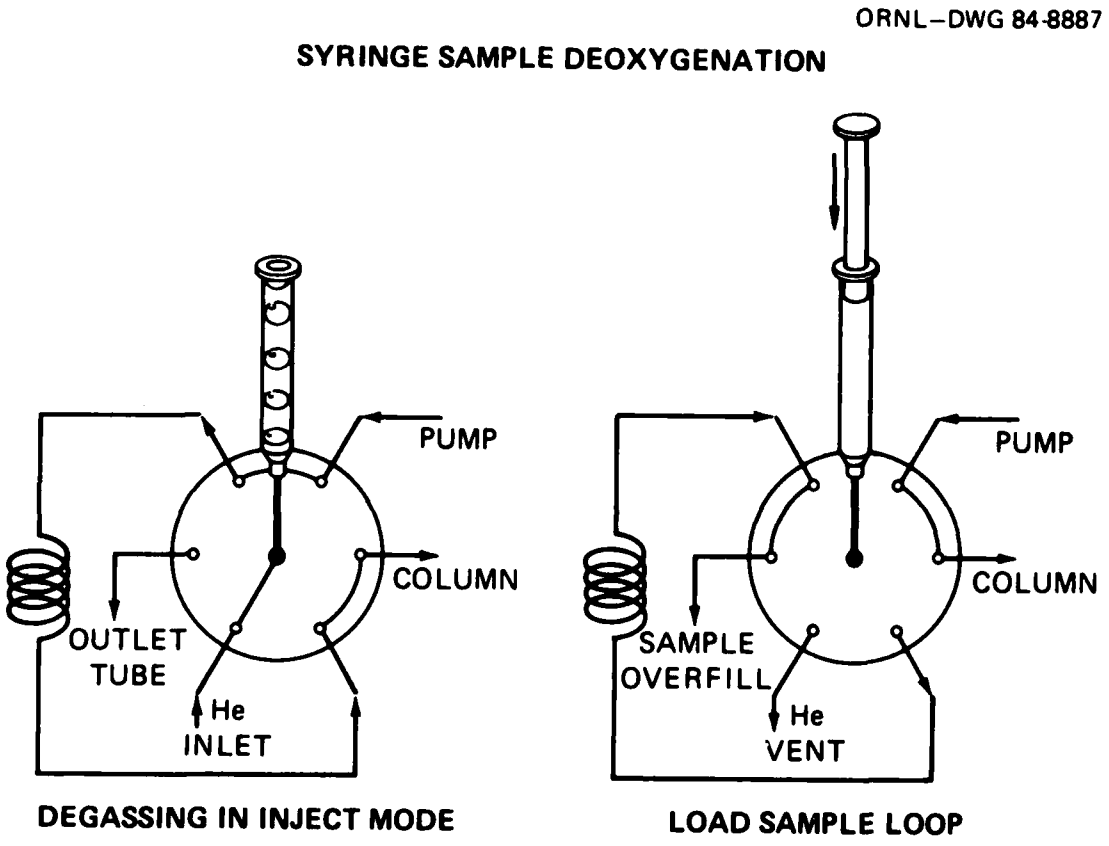

Figure 4. Syringe Sample Deoxygenation

of the controller is carried out as per instructions. Additional instructions for the BAS detector, end-of-day:

1. Leave voltage on working electrode.
2. Adjust mobile phase flow to 0.1 mL/min.
3. Set recorder to standby.

For shut-down:

1. Set controller to standby.
2. Reduce voltage to zero.
3. Turn off compensation circuits.
4. Turn off pumps.
5. Set recorder to standby.
6. Remove reference electrode, store in 3 M NaCl.

Additional instructions for the PAR detector, end-of-day:

1. Store capillary in distilled water.
2. Turn off flow of mobile phase.
3. Set cell selector switch to OFF.
4. Set recorder to standby.

For shut-down:

1. Set cell selector switch to OFF.
2. Turn off pumps.
3. Turn off compensation circuits.
4. Store capillary in distilled water.
5. Set recorder to standby.
6. Turn off inert gas flow to the polygraphic detector.

RESULTS AND DISCUSSION

Development of the HPLC Analytical Method

Our first efforts were to utilize UV detection for measurement of the explosives following resin isolation and liquid chromatographic separation. Nitroglycerin and PETN were to be detected at 210 nm while HMX, RDX, TNT, 2,4-DNT, 2,6-DNT, and TETRYL were to be detected at 254 nm. No insurmountable difficulties were encountered in the separation and detection of stock solutions of standards (Figure 5). However, when the explosives were subjected to sorption and desorption from the resins (Porapak-R, Porapak-S), troublesome background and extraneous peaks severely hampered reliable measurements with the UV detectors (See Figure 6).

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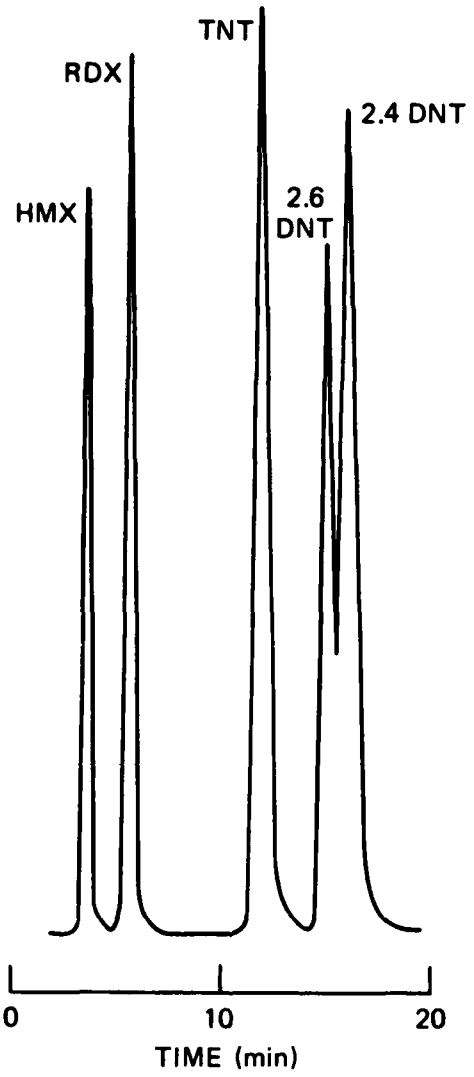


Figure 5. Chromatogram of Explosive Compounds

Column:	Spherisorb (ODS) 5u
Mobile Phase:	Methanol:Water (50:50) 1 mL/min
Injection Volume:	50 uL
Detection:	UV 254 nm 0.05 AUFS
HMX, RDX, TNT,	20 ug/mL
2,6-DNT, 2,4-DNT	10 ug/mL

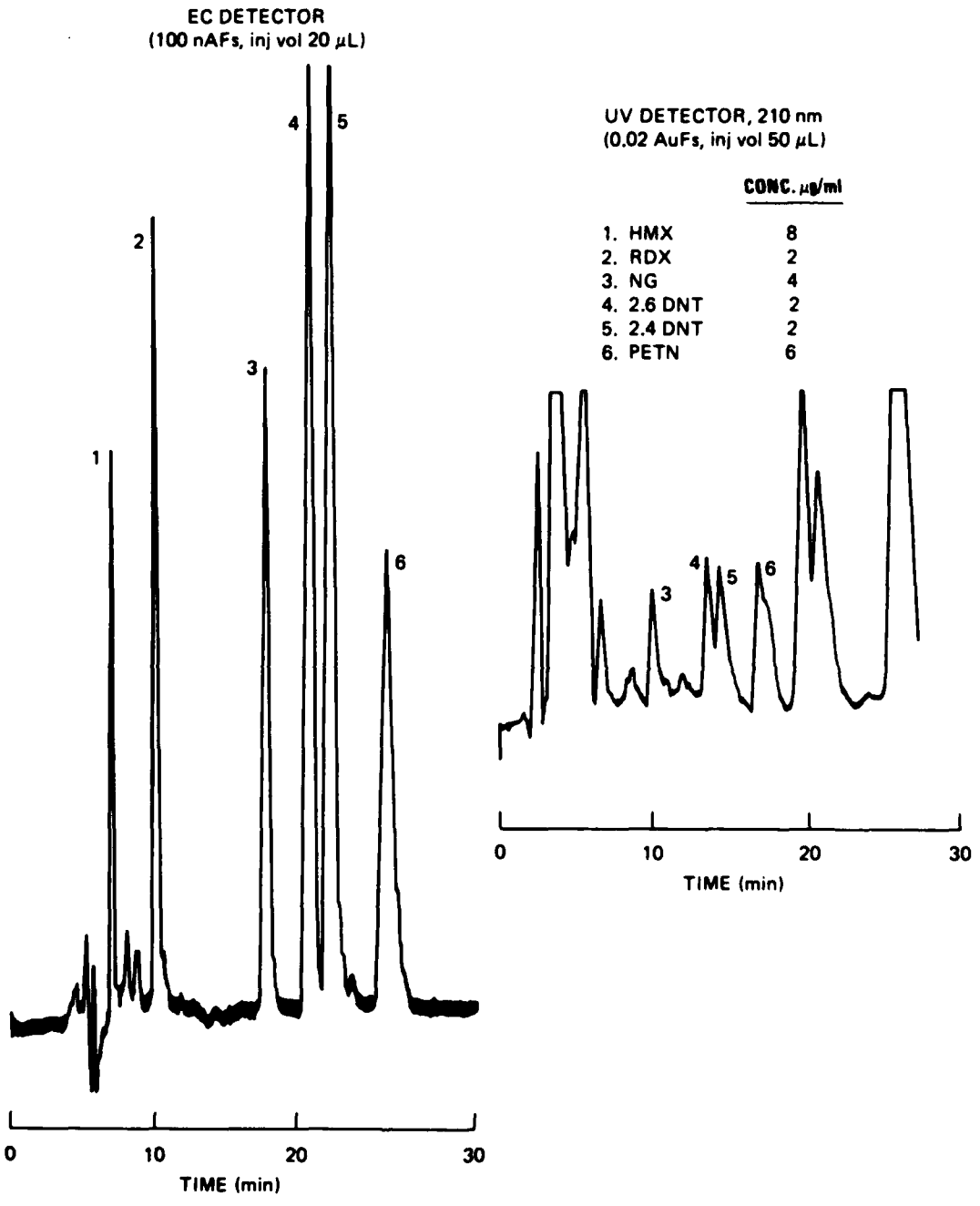


Figure 6. Electrochemical and Ultraviolet Detection of Explosives Following Adsorption and Desorption Using Porapak-R

This was puzzling in view of the fact that in earlier work (8) a UV detector at 204 nm was used for the analysis of NG and PETN with no such interference from the resin. The interferences encountered here could have been attributed to two sources: 1) batch variation in the resins, or 2) normal phase separations were performed earlier in contrast to our reverse phase separation. Even though the resins were cleaned according to the previous procedure (8), several experiments were performed in order to reduce the background. The results are summarized as follows:

1) Cleaning the resins in-situ after packing the cartridges reduced the background in all three resins.

2) It was found that background could be consistently reduced by not allowing the resin to dry out.

3) Regardless of type of treatment, the background was consistently highest on XAD-4, followed by Porapak-R and Porapak-S.

After these steps had been taken, the resin background could be reduced to a point where the compounds which absorb at 254 nm could be determined. However, as might be expected NG and PETN were still prone to interferences (detected at 210 nm). The alternative separation on normal phase columns was ruled out since actual samples would be difficult to handle reproducibly in the normal phase mode because of the water content. Additionally, the sensitivity for the various compounds was widely variable depending on spectral properties.

In view of these difficulties, electrochemical detection was considered as an alternative for the determination of these explosives. The amperometric detector is operated in the reductive mode at -1.0 volts versus Ag/AgCl working electrode. The technique employed for reductive mode applications, i.e., all stainless steel system and oxygen-free mobile phase, is similar to that of Bratin, Kissinger, et al. (19,20). The syringe deoxygenation of small samples is a modification of the method proposed by LLoyd (21).

Electrochemical detection is more sensitive and selective than UV detection. Thus, the troublesome and non-reproducible background peaks should be of less consequence. Nevertheless, the sample injected onto the column should be reasonably clean, as non-electroactive species may be specifically adsorbed at the electrode surface, resulting in erratic detector behavior.

Chromatograms illustrating electrochemical and ultraviolet (210 nm) detection of explosives following adsorption and desorptions using Porapak-R are shown in Figure 6. The worrisome background encountered by the UV detector was not as severe with the EC

detector. The UV background from the resins was much reduced at 254 nm, however, the HMX and RDX peaks were often not resolved from the interference peaks, particularly when working at low concentrations.

Dupont Zorbax ODS (5 um) columns were the most often used. The resolution of the 2,4-DNT and 2,6-DNT peaks was consistently better on these columns. An HPLC/EC chromatogram for the separation of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN is shown in Figure 7. The resolution of the TNT and NG peaks are good on a new column, although the separation deteriorates as the column ages. By using a weaker mobile phase, the separation can again be achieved, although the resolution of the DNT peaks is compromised. If the separation of TNT and NG is not of interest, good resolution of the explosives can be achieved without changing the mobile phase. The elution of HMX occurs close to the solvent front and is therefore prone to interferences, particularly at low concentrations.

The PAR detector is the more useful system for the reductive HPLC-EC analysis of explosives, especially where throughput is of concern. Electrode renewal is not a problem, although we have experienced capillary fouling with prolonged use. In the case of the BAS electrode, the main difficulty was the variability of the useful lifetime of the electrode. The lifetimes varied from as long as 2-3 weeks to as short as a few days. This variability places the electrode at a disadvantage with respect to the HMDE, which can be formed immediately before analysis.

An advantage of the BAS dual electrode system is the ability to assess peak purity by monitoring the column effluent at two potentials simultaneously. The potentials are chosen so that E_1 will be on the limiting current plateau and E_2 somewhere along the reduction wave of the component. Thus, the ratios of the peak currents (i_1/i_2) are used to assess purity of the peak in much the same way as the dual wavelength UV detector is used.

The explosive response factors were lower at the HMDE than at the Au/Hg electrode, due in part to the smaller surface area of the HMDE. However, background current and noise were also lower, such that the signal/noise ratios for the two detectors were comparable under our operating conditions.

Good results were obtained with each resin (and solvent extraction) for HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN in laboratory water (see Appendices). Tetryl was best recovered from aqueous solutions by adsorption on XAD-4. In the case of tetryl the acetone eluates for the resin must be analyzed as quickly as possible, since the tetryl is not stable in acetone for extended periods (days). This is illustrated in Figure 8 where the upper chromatogram shows the an acetone extract of explosives analyzed immediately after desorption. The lower chromatogram represents the analysis of the same extract 5

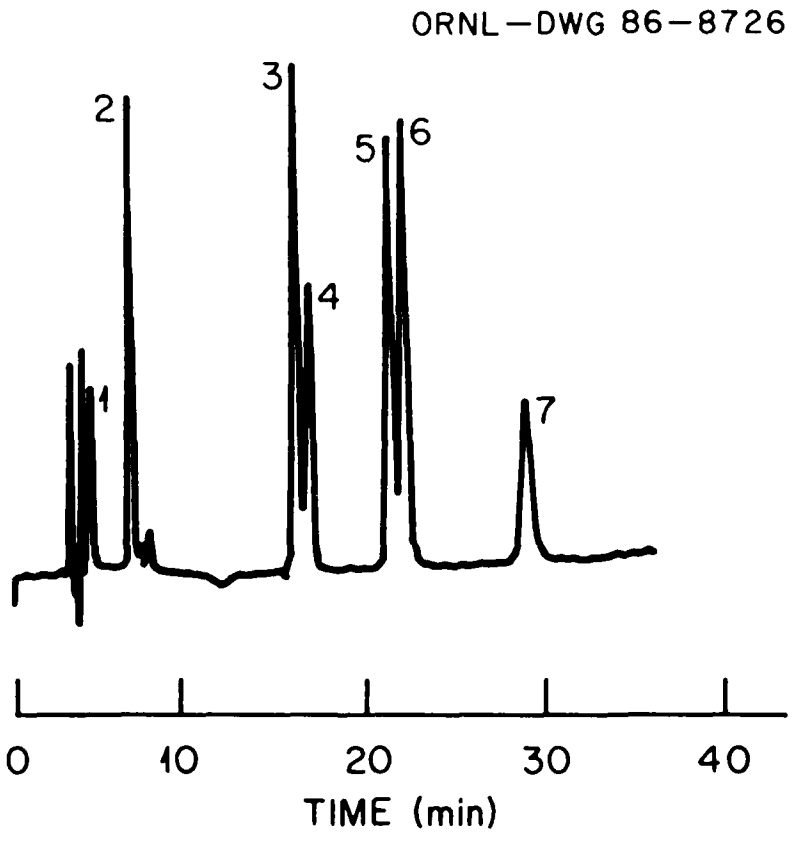


Figure 7. Separation of Explosives by HPLC/EC

1. HMX
2. RDX
3. TNT
4. NG
5. 2,6-DNT
6. 2,4-DNT
7. PETN

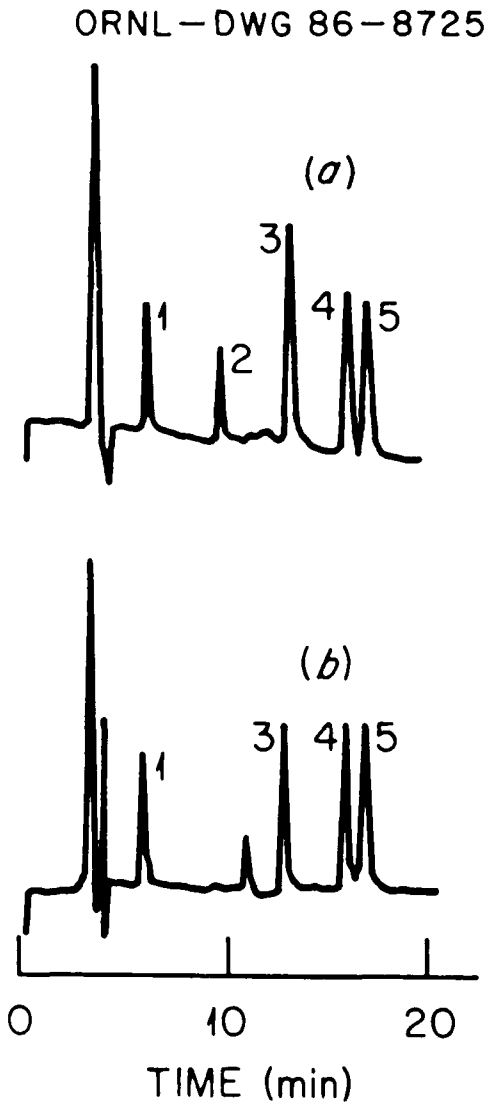


Figure 8. HPLC/EC Separation of Explosives in Acetone Eluant from XAD-4 Adsorbent

(a) Explosives desorbed and analyzed the same day.
(b) Extract chromatographed after five days aging.

Peak	Explosive
1	RDX
2	Tetryl
3	TNT
4	2,6-DNT
5	2,4-DNT

Mobile Phase: N prop: .025 M NgAc (30:70) pH 6 w/HAc
Flow rate: 0.8 mL/min
Column: DuPont Zorbax ODS (5u)
Inj. vol.: 20 uL
MHDE @ -1 V vs Ag/AgCl reference electrode
50 nafs
Conc., 0.4 ug/mL

days later. The Tetryl peak has completely disappeared. All other explosives have reasonable stability.

We also observed that aqueous solutions of tetryl do not appear to be stable (Figure 9). In this case, the solutions of tetryl appear to have undergone some form of degradation, as evidenced by the appearance of additional peaks in the chromatogram. However, it did appear that the tetryl exhibited good stability in ethanol. In real samples, multiple tetryl peaks will likely occur. However, this will not affect the determination of tetryl as long as the reference compound is freshly prepared.

Due to the high polarity of nitroguanidine, none of the resins tested were able to collect and retain this compound. Solvent partition failed as well. However, it was possible to concentrate water samples containing nitroguanidine by rotary evaporation. As noted in Figure 10, the separation of this compound required a substantially weaker mobile phase, as well as a reduced flow rate, particularly for the separation of nitroguanidine from HMX and RDX. Even under these conditions, nitroguanidine is not well retained by the column and elutes first. For aqueous samples containing other polar components, interferences can be a problem. From the detection standpoint, nitroguanidine was the most difficult explosives to reduce. The reduction potential was -1.2 Volts vs Ag/AgCl. This negates, to some extent, the selectivity of the electrochemical detector.

Analysis of Samples from Volunteer Army Ammunition Plant (VAAP)

In order to validate the methodology for field sampling purposes, three samples were acquired in 1 gal amber jugs from VAAP. An attempt was made to acquire samples with widely varying concentrations. Samples were collected from two wells, well #3 and well #11. The third sample was an aliquot from well #3 which had been filtered to investigate particle sorption of explosives. For each sample, 250 mL was pumped through Porapak-R at ca. 5 mL/min, eluted with acetone and analyzed for dinitrotoluenes and TNT by HPLC/EC. Results are shown in Table 1.

Table 1. Analysis of VAAP Well Waters for TNT, 2,6-DNT, and 2,4-DNT (ug/L)

Component	Sample #3		Sample #1
	Filtered	Unfiltered	Unfiltered
TNT	13	11	2.8
2,6-DNT	138	155	3.0
2,4-DNT	266	276	2.7

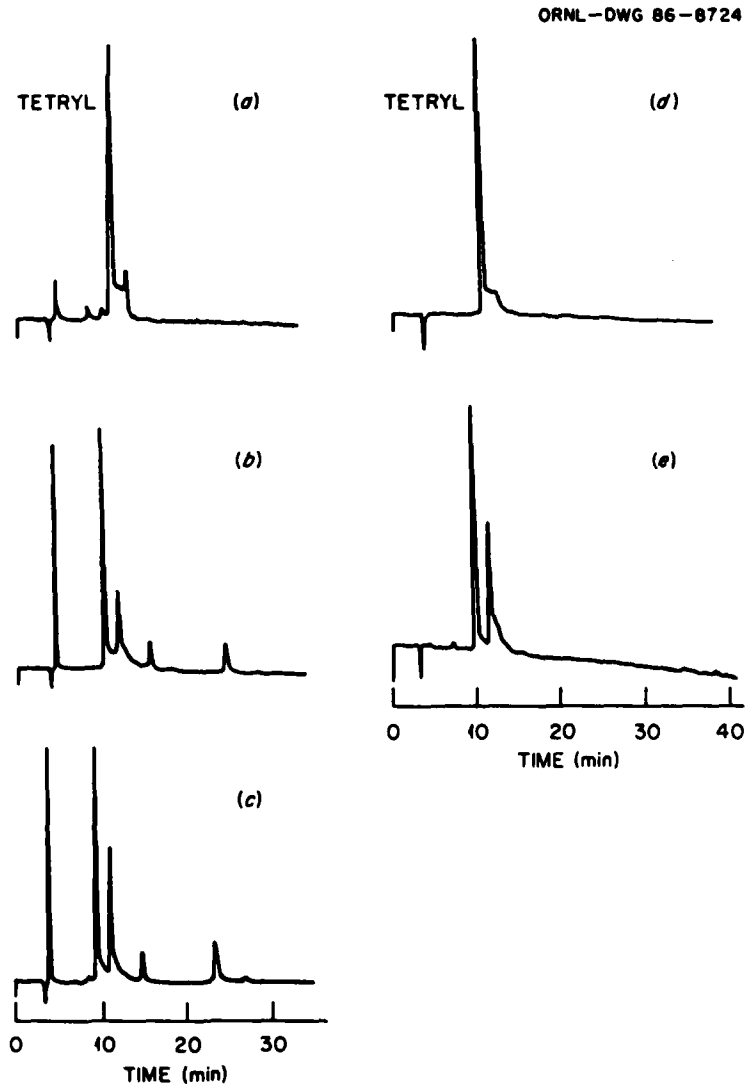
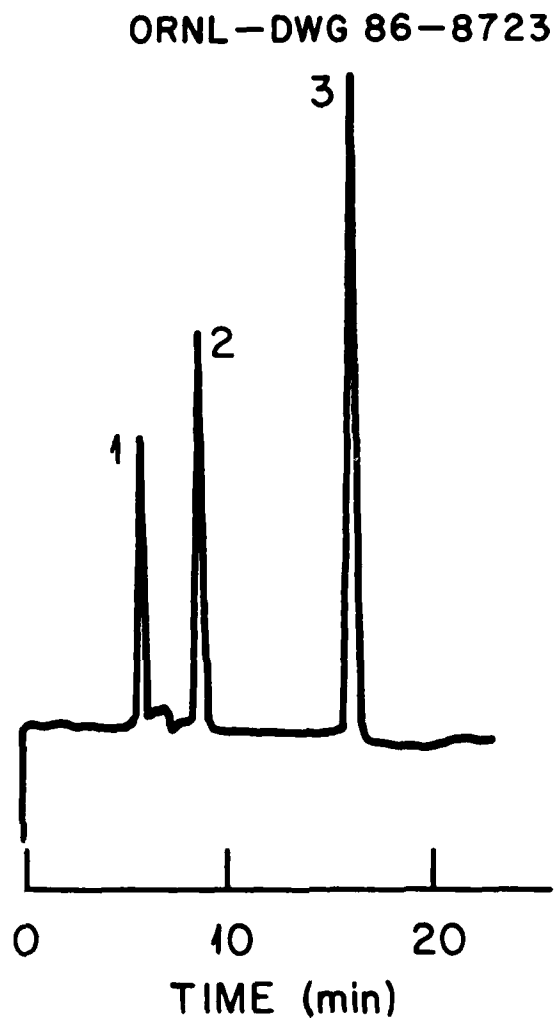


Figure 9. HPLC/EC Chromatograms Showing Effect of Aging on Aqueous Solutions of TETRYL. Concentration ~2 ug/mL.

(a) Freshly prepared from old stock solution of Tetryl.
(b) Three weeks aging.
(c) Five weeks aging.
(d) Freshly prepared from new stock solution of Tetryl.
(e) Two weeks aging.

HPLC/EC conditions per Figure 8.



Column:	DuPont Zorbax ODS (5u)
Mobile Phase:	1-propanol: 0.025 M Acetate buffer, pH 6, (20:80)
Flow:	0.5 mL/min
Inj. Vol.:	20 uL
Detection:	Au/Hg electrode @ -1.2 V vs Ag/AgCl
Peak:	1. Nitroguanidine
	2. HMX
	3. RDX

Figure 10. HPLC Separation of Nitroguanidine, HMX, and RDX with Electrochemical Detection

It did not appear that any procedural difficulties would be encountered in the application of resin adsorption to field samples at least when the sorption was achieved in the laboratory. Detection limits for these substances of 1 ug/L were achieved.

Furthermore, no appreciable difference between the filtered and unfiltered sample was found. This indicated that an option existed. If filtration can be accomplished conveniently, it would be useful to do so, in that the pump performance would be much improved. However, filtration is not a necessity.

A sampling trip to VAAP was conducted in order to assess the practicality of the sampling protocol in the field. Battery operated pumps were used to adsorb samples immediately after collection at the well. This approach proved imprudent, due to inconsistent pump operation, temperature fluctuation, and flow rate variations. After one sample was collected all remaining samples were returned to the laboratory (at VAAP) and the resin adsorption performed there. Eight well samples were collected. Samples from Well #3 known to contain nitrotoluenes were used to compare Porapak-R and S. Four aliquots were drawn through columns of Porapak-R and one aliquot was drawn through Porapak-S. The results are shown in Table 2.

Table 2. Repetitive Analysis of TNT, 2,6-DTN, and 2,4-DNT on VAAP Well #3 (ug/L)

	Porapak-R				Porapak-S
Component	1	2	3	4	1
TNT	14.1	17.6	17.6	15.8	14.7
2,6-DNT	107	78	85	85	71
2,4-DNT	213	166	186	199	152

As noted from Table 2, the reproducibility of the Porapak-R data is quite good. In general, the values are somewhat higher than the values obtained from Porapak-S.

Three samples from Well D which contained low levels of nitrotoluenes was used to compare Porapak-R, Porapak-S, and solvent extraction technologies. These results are shown in Table 3.

Table 3. Analysis of TNT, 2,6-DNT, and 2,4-DNT in VAAP Well "D" (ug/L)

Component	Porapak-S	Porapak-R	Solvent Partition
TNT	1.5	1.0	3.3
2,6-DNT	3.0	2.0	5.9
2,4-DNT	8.0	11.9	13.5

For this sample, the Porapak resins yielded lower results than did the solvent extraction. The cause of this discrepancy is unknown, although a proper statistical treatment cannot be done due to the lack of replication. Two aliquots of Well #3 sample were spiked with HMX, RDX, and PETN. However, the high concentrations of the nitrotoluenes prevented the measurement of these components near the detection limit. Therefore, the analytical protocol for field evaluation of this methodology was modified as follows:

1) No further "spiking" was done on field samples containing explosives components.

2) Each field sample was isolated in triplicate on each resin.

3) At least one sample was identified as background, and this sample was used to spike with known quantities of explosives.

4) All resin isolations were done in the laboratory of the facility being sampled. Samples were collected with a bailer and stored in 4 L amber jugs until processing.

Analysis of Samples from Milan Army Ammunition Plant (MAAP)

The purpose of the sampling trip to MAAP was to further evaluate the resin sorption technologies on real-world samples. This effort was aided considerably by the availability of analytical facilities on-site for the characterization and quantitation of the collected samples. Water samples from each of the collection points at MAAP

were analyzed by HPLC on site. A 200 uL injection of the water itself onto a reverse phase column with UV detection at 245 nm gave detection limits of 10 ug/L. The DNT isomers were not resolved. The results are shown in Table 4. Well MI-056 and O-Line pond #5 were spiked with TETRYL, NG, and PETN in addition to the normal protocol. Thus, information on the recovery of these components from real samples was obtained.

Table 4. Concentration of Munitions Components in Samples Collected At Milan Army Ammunition Plant (ug/L). Samples Analyzed Directly On-Site

Sample	HMX	RDX	TNT	DNT
O-Line Pond #5	15.6	111.1	<10	<10
S-4 Boundary	<10	<10	<10	<10
MI 010 Well	12.2	79.8	13.4	<10
MI 001 Well	2,110	26,300	11,500	82.6
MI 056 Test Well	<10	11.9	<10	<10
MI 002 Well	<10	46.4	60.8	<10
K-100 Well	<10	313	213	3.1

A wide variety of samples were collected. The O-Line Pond sample represents a contaminated, standing surface water. The S-4 boundary sample represents an uncontaminated flowing surface water. The wells MI-001, MI-002, MI-010, and MI-056 represent RCRA monitoring wells (ground water) with a wide range of component concentrations. Well K-100 represents a contaminated potable well.

This wide variety of samples allowed for several experiments to be performed. In order to ensure the quality of the analyses, triplicate QC standards (explosives spiked into laboratory water) were isolated by each technique. As shown in Table 5, the results were, for the most part, very good.

Table 5. Recovery of Standard Explosives from Milan Laboratory Water (QA STDS) (n=3)

QA STD #1 Recovery (%)

Method	HMX	RDX	TNT	2,6-DNT	2,4-DNT
Porapak-R	89.7	93.6	78.5	100.5	112.8
Porapak-S	76.2	90.3	63.1	95.9	106.7
XAD-4	67.2	87.2	75.9	97.4	107.1
Solvent Extract	95.0	84.6	4.6(?)	62.0	57.9

QA STD #2 Recovery (%)

Method	HMX	RDX	NG	PETN
Porapak-R	103.5	127.9	134.9	141.1
Porapak-S	111.3	118.5	116.9	111.9
XAD-4	94.4	94.1	115.9	101.6
Solvent Extract	103.1	89.6	65.4	97.8

QA STD #1: 20 ug/L HMX, RDX, TNT, and 10 ug/L 2,6-DNT, 2,4-DNT
QA STD #2: 40 ug/L HMX, RDX, NG, PETN

The low level of contamination in the O-Line pond sample and in the Well MI 056 allowed the use of these samples for standard addition purposes. The results of this experiment are shown in Table 6. The recovery of the components was consistent but somewhat lower than that attained using distilled water. There did not appear to be a significant difference in the performance of the resins for these samples, nor was there a significant difference between the recoveries from surface water and groundwater.

Table 6. Recovery of Standard Additions of Explosives from O-Line Pond #5 and Test Well 056

Method	O-Line Pond 5* Recovery, Percent (N = 2)			
	NG	2,6 DNT	2,4 DNT	PETN
Porapak-R	71.5 ± 2.8	51.2 ± 17.3	54.4 ± 12.0	73.3 ± 16.8
Porapak-S	82.9 ± 0.6	55.3 ± 2.2	65.2 ± 1.7	88.4 ± 0.1
XAD-4	51.6 ± 18.9	74.9 ± 13.2	81.5 ± 17.6	74.8 ± 17.8
	Well 056** Recovery, Percent (N =2)			
Method	HMX	RDX	NG	PETN
Porapak-R	94.7 ± 2.8	78.2 ± 13.0	57.4 ± 34.5	68.4 ± 26.7
Porapak-S	118 ± 5	65.9 ± 24.3	63.9 ± 1.5	79.3 ± 1.6
XAD-4	96.3 ± 20.7	57.5 ± 2.6	49.6 ± 3.2	47.8 ± 1.4
Solv Ext (N=1)	135	80.2	64.9	79.5

*16 ug/L NG, 8 ug/L 2,6-DNT, 2,4-DNT, and 24 ug/L PETN.
**40 ug/L HMX, RDX, NG, PETN.

The sum total effort at MAAP resulted in the collection of ca. 90 samples on resin cartridges in 1.5 days using six pumps. Several observations on the behavior of the resins were made during the sampling trip:

1) XAD-4 provides less back pressure than the Porapaks, resulting in higher flow rates, but also less flow control. The Porapaks are more or less equivalent.

2) With any of the resins, about 8 samples/day can be collected with each pump.

The extremely high levels of explosives in MI-001 made this sample appropriate for assessing the relative capacity of the three resins. The experiment was performed as follows: The sample was analyzed prior to passing through the resin and the eluent reanalyzed. The breakthrough data are shown in Table 7.

It is clear that the Porapak resins outperform the XAD-4 in terms of capacity for the components in this sample. However, more important is the relative behavior of each resin toward the components. The XAD-4 behaves in a nonspecific manner. Adsorption on the XAD-4 is related primarily to hydrophobicity. Thus, breakthrough of HMX is greatest, followed by RDX, followed by TNT. This is precisely in decreasing order of polarity. On the other hand, the Porapaks appear to behave in a manner consistent with specific adsorption of nitro groups - the breakthrough being more or less equivalent for the four components. The implications for field sampling are that the XAD-4 capacity will be much more related to the total organic load than to the total explosives load, while the capacity of the Porapaks will be more related to the total explosives load.

The results of the remaining MAAP samples are shown in Table 8. While the samples were analyzed for all components, only values above the detection limit are shown. As noted earlier, the most contaminated sample was MI 001 well, while only a small amount of RDX was found in S-4 creek, the least contaminated sample. These represent a concentration range of four orders of magnitude. Where comparisons could be made with on-site measurements, the results were in reasonable agreement. For the more contaminated samples, values for RDX were somewhat lower than the on-site measurements, but generally consistent among the four methods. For Well 056, from which a relatively clean sample was taken, the agreement among the four methods and with the on-site measurement for RDX was good. Values for HMX were generally higher than the on-site values. It is not certain if this difference is due to the different calibration standards used in the two laboratories or to differences in the chromatographic resolution. The HMX peak is not well resolved from the solvent front in either system. However, the standard deviation is about the same as for the other peaks.

Generally, XAD-4 and solvent extraction produced somewhat lower HMX values than the Porapak adsorbents. The four methods gave consistent values for TNT and DNT and, where possible, agreements with on-site values were very good.

Table 7

Resin Breakthrough Studies Using Water from Well MI 001

Component	Concentration in water, ug/L[b]	Breakthrough for Resin: XAD-4[a] Conc., ug/L[b]	XAD-4[a] Percent[c]	Porapak R[d] Conc., ug/L[b]	Porapak R[d] Percent[b]	Porapak S[e] Conc., ug/L[b]	Porapak S[e] Percent[c]
HMX	2,110	815	39	<10	<0.5	34.5	1.6
RDX	26,300	6940	26	7.4	0.03	391	1.5
TNT	11,500	1490	13	6.6	0.06	<10	<0.09
DNT	82.6	<10	<12	<10	<12	<10	<12

[a]Average for n=3.

[b]Concentration in water after passing through cartridge. "<10" means not detected, but limit of detection used to calculate upper bound on breakthrough.

[c]Percent breakthrough = conc. in water passed through cartridge/conc. in original sample x 100%.

[d]Average for n=2.

[e]Result for n=1.

Table 8

Analysis of Explosives in Test Samples

Sample	Method	Concentration ug/L (Avg. N=3) HMX	RDX	TNT	2,4-DNT
MI 001 Well					
	Porapak-R	3690 ± 390	15000 ± 1450	10200 ± 1610	93.2 ± 12.4
	Porapak-S	3650 ± 334	15400 ± 1510	10400 ± 852	101.4 ± 13.6
	XAD-4	3390 ± 700	19500 ± 832	12200 ± 4060	95.2 ± 13.6
	Solv Ext	1630 ± 185	12500 ± 1612	11300 ± 1840	105.3 ± 11.6
	Direct*	2110	26300	11500	82.6

		ug/L (Avg. N=3) HMX	RDX	TNT	2,4-DNT
Well K-100					
	Porapak-R	39.3 ± 4.0	193 ± 24	223 ± 4	4.8 ± 0.5
	Porapak-S	23.5 ± 1.6	198 ± 19	218 ± 22	3.2 ± 0.3
	XAD-4	19.0 ± 2.3	156 ± 19	178 ± 28	2.8 ± 0.1
	Solv Ext	15.5 ± 0.8	185 ± 15	213 ± 8	3.5 ± 0.6
	Direct*	<10	313	213	3.1

		ug/L (Avg. N=3) HMX	RDX	TNT	2,6-DNT	2,4-DNT
MI 002 Well						
	Porapak-R	8.6 ± 1.6	33.4 ± 3.6	61.7 ± 9.3	1.3 ± 0.5	1.2 ± 0.2
	Porapak-S	11.8 ± 1.3	34.1 ± 7.2	79.0 ± 8.8	1.9 ± 0.6	1.5 ± 0.4
	XAD-4	10.2 ± 1.5	32.1 ± 6.2	63.7 ± 6.3	0.8 ± 0.2	0.7 ± 0.2
	Solv Ext	6.1 ± 0.1	29.7 ± 6.0	60.2 ± 12.3	1.6 ± 0.6	1.2 ± 0.6
	Direct*	<10	46.4	60.8	<10	<10

(Cont'd)

Table 8 (Cont'd)

Analysis of Explosives in Test Samples

Sample	Method	Concentration ug/L (Avg. N=2) HMX	RDX	TNT
O-Line Pond 5				
	Porapak-R	30.0 ± 1.8	79.0 ± 3.4	0.8 ± 0.3
	Porapak-S	34.6 ± 10.2	91.8 ± 26	0.9 ± 0.2
	XAD-4	24.8 ± 1.1	65.8 ± 4.5	2.0 ± 0.9
	Direct*	15.6	111	<10

Sample	Method	ug/L (Avg. N=3) RDX
Well 056		
	Porapak-R	10.5 ± 1.1
	Porapak-S	13.1 ± 1.5
	XAD-4	11.6 ± 3.0
	Solv Ext	12.6 ± 0.2
	Direct*	11.9

Sample	Method	ug/L (Avg. N=3) RDX
S-4 Creek		
	Porapak-R	3.0 ± 0.4
	Porapak-S	3.3 ± 0.6
	XAD-4	2.6 ± 0.6
	Solv Ext	2.9 ± 0.5
	Direct*	<10

*On-Site

3) The lack of breakthrough on Porapaks-R and S suggested that a change in geometry of the cartridge to promote higher flows may be possible. This would allow a shorter time for resin sorption, and more samples to be collected per day.

4) Only in rare cases of gross particulate contamination will it be necessary to prefilter the sample.

Analysis of Samples from Holston Army Ammunition Plant (HAAP)

A sampling trip was made to HAAP in order to build on the data obtained at Milan. The purposes of this trip were:

1) To ensure that the resin behavior observed at Milan would be generally applicable.

2) To assess the applicability of the resin technology to process waters (not sampled at Milan).

3) To assure the applicability of the resin technology to groundwater in an area with clay soil.

Again, standard additions were made to the HAAP laboraory water. The recovery data are shown in Table 9. The recovery was in general quite good. As was the case at Milan, analytical facilities were available for the characterization of the samples on-site with a detection limit of 50 ug/L. Three samples were collected: inlet and outlet wastewater and a groundwater.

Table 9. Percent Recovery of Standard Explosives from Holston Laboratory Water (QA STDS) (N=2)

Method	HMX	RDX	TNT	2,6-DNT	2,4-DTN	PETN
Porapak-R	118	89	50	81	100	125
Porapak-S	132	122	63	60	90	120
XAD-4	102	76	66	29	58	76
Solv Ext	175	118	89	88	88	101

10.0 ug/L HMX, RDX, TNT, 2,6-DNT, 2,4-DNT, PETN

In addition to RDX, the process streams contained HMX, SEX (acetylated HMX) and TAX (acetylated RDX). Under our chromatographic conditions, these latter three substances were not resolved. The SEX and TAX coeluted with the HMX, producing a large single peak close to the solvent front on the chromatogram.

However, under the conditions used at HAAP, all of these substances could be quantitatively analyzed. Therefore, a breakthrough study was carried out similar to that done at Milan. The results are given in Tables 10 and 11. The groundwater sample was not analyzed due to the expectation that no contamination was present.

Table 10. Breakthrough Studies Using HAAP Raw Inlet Water

Component	Conc. (ug/L)	Resin Breakthrough					
		XAD-4		Porapak-R		Porapak-S	
		Conc[a]	%[b]	Conc[a]	%[b]	Conc[a]	%[b]
SEX	3400	3200	94	260	7.6	800	24.0
TAX	1300	740	57	60	4.6	180	13.8
HMX	2500	820	33	<50	2	100	4
RDX	1300	540	42	<50	4	<50	4

[a] Concentration in water after passing through cartridge (ug/L). "<50" not detected, but used to calculate upper bounds on break through.

[b] % = conc. x 100 in water passed through cardridge/conc.in original water.

As is clear from the data, the same trends were observed here as have previously been discussed with respect to the MAAP samples. It is interesting that the Porapak resins were able to effectively sorb even the polar SEX and TAX, even at mg/L levels.

The results of the analysis of RDX in the HAAP samples is shown in Table 12. Better agreement was attained in this case than in the case of the MAAP samples.

Table 11. Breakthrough Studies on HAAP Effluent Water

Component	H_2O Conc. (ug/L)	Resin Breakthrough					
		XAD-4		Porapak-R		Porapak-S	
		Conc[a]	%[b]	Conc[a]	%[b]	Conc[a]	%[b]
SEX	5030	3000	60	160	3.1	890	18
TAX	960	680	71	<50	5.2	160	17
HMX	440	220	50	<50	8.8	<50	8.8
RDX	230	100	43	<50	22	<50	22

[a] Concentration in water after passing through cartridge (ug/L). "<50" not detected, but used to calculate upper bounds on break through.

[b] % = conc. x 100 in water passed through cartridge/conc. in original water.

The measurements of HMX, RDX, and TNT in Holston groundwater are also shown in Table 12. The levels are quite low, <200 ppb HMX and RDX, and <50 ppb TNT. The HMX peak was counted as HMX although it could result from a mixture of HMX, SEX and TAX. Standard additions of HMX, RDX, NG and PETN were made to aliquots of this groundwater sample to check recoveries. However, not knowing beforehand the base-line levels of these substances, not enough standard was added to significantly change the overall concentrations, except for PETN. The recoveries of PETN from Porapak-R, Porapak-S, and XAD-4 were 70, 82 and 50 percent, respectively, (N=2).

Thus, the trends in sample handling techniques observed at Milan were also applicable to samples at the HAAP. The only exception was that the groundwater collected from HAAP required filtration prior to sorption.

Analysis of Samples from Sunflower Army Ammunition Plant (SAAP)

Various water samples from SAAP were shipped to ORNL and analyzed for nitroguanidine in order to further validate the methodology developed for this compound. While no reference data are available, no

problems were encountered with the method and the data generated are within historical limits for similar samples at SAAP. The results are presented in Table 13.

Table 12. Analysis of RDX in HAAP Inlet and Outlet Process Streams

	RDX, ug/L (N = 3)	
Method	Inlet	Outlet
Porapak-R	1700 ± 246	200 ± 68
Porapak-S	1880 ± 45	280 ± 15
XAD-4	1010 ± 263	170 ± 37
Solv Ext	580 ± 247	260 ± 8

Analysis of HMX, RDX and TNT in HAAP Groundwater

	Conc, (ug/L) N = 3		
Method	HMX	RDX	TNT
Porapak-R	123 ± 16	142 ± 3	42 ± 26
Porapak-S	162 ± 32	120 ± 44	23 ± 2
XAD-4	107 ± 38	105 ± 3	23 ± 4

Sample 1 was analyzed directly. Samples 2-6 were analyzed after concentration. Sample 7 was diluted by a factor of 10 prior to analysis. A large, early-eluting peak due to an electroactive substance more polar than nitroguanidine was noted in Sample 2 (Figure 11). The sample contained only a single peak [chromatogram (a)]. After addition of nitroguanidine to the sample and reanalysis, it is clear that the nitroguanidine [chromatogram (b)] is separated from the interference. However, the resolution obtained is not adequate for unambiguous determination of the nitroguanidine. It is recommended that the method of standard additions be used for quantification in such cases. It is worth noting that the interferences may be either organic or inorganic in nature.

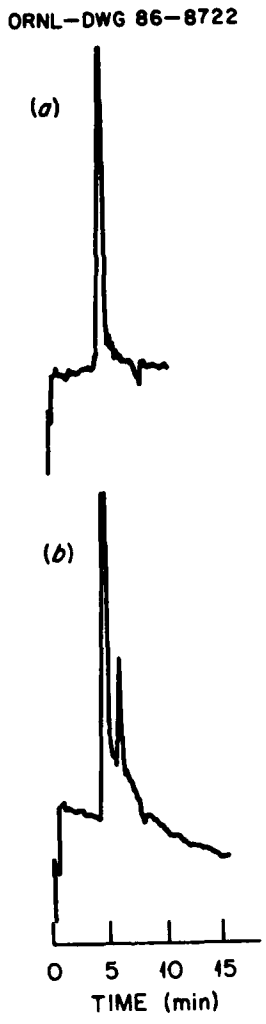


Figure 11. HPLC/EC Chromatogram on SAAP Water Sample Number Two

Table 13. Analysis of Water samples from SAAP for Nitroguanidine

SAMPLE NUMBER	IDENTIFICATION	[NITROGUANIDINE]
1.	NSE outfall	4.7 ± 0.4
2.	NQ cooling tower	<0.04
3.	Tank T-784	<0.04
4.	S-1 surface water	0.05 ± 0.02
5.	D9042sump	0.31 ± 0.07
6.	C9017 sump	0.08 ± 0.03
7.	D9017 sump	2140 ± 220

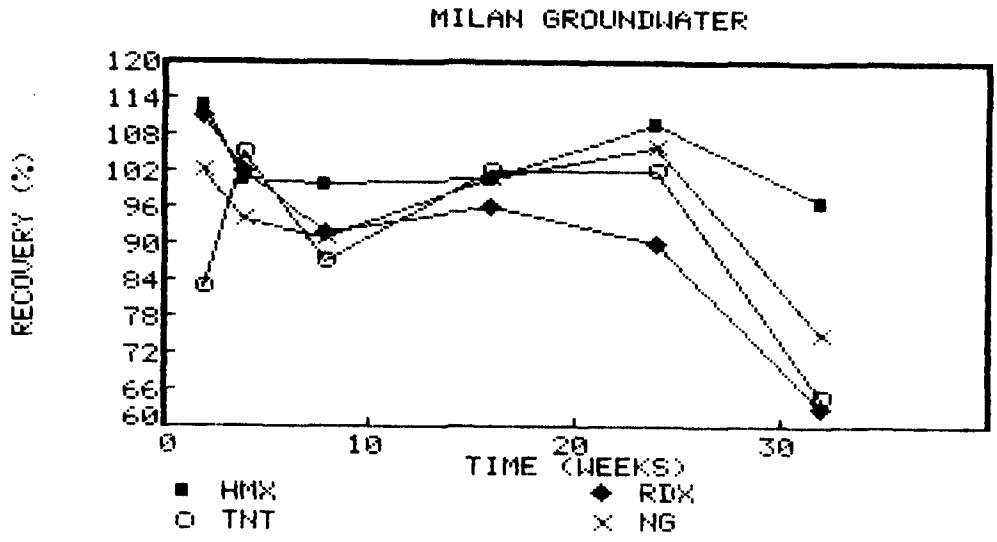
[Nitroguanidine] = mg/L
N = 3

Stability of Explosives Adsorbed on Porapak-R

A study was carried out to define the storage stability of various explosives when sorbed onto Porapak-R and stored at 4°C. Three samples were collected in bulk for this study:

1. A groundwater sample from MAAP.
2. A groundwater sample from VAAP.
3. A groundwater sample from ORNL.

No explosives were present in the samples initially. The samples were spiked with HMX, PETN, NG, RDX, TNT, 2,6-DNT, and 2,4-DNT. 250 mL samples were passed through Porapak-R and analyzed at the following intervals: 1, 2, 4, 8, 16, 24, and 32 weeks. The purpose of this study was to define an "expiration date" after which the samples could not be considered reliable. All data points were collected in triplicate. The results are shown graphically in Figures 12-14. Except for minor fluctuations, the explosives appear to exhibit excellent stability long-term on the Porapak-R. The recovery of TNT was the most variable, particularly in the ORNL and VAAP groundwaters. These waters were of higher pH than the MAAP groundwater (7.2 & 7.6 vs 6.6). It is difficult to explain the reduced recovery solely in terms of the pH, although the differences between the samples could be more complicated than simply pH. It



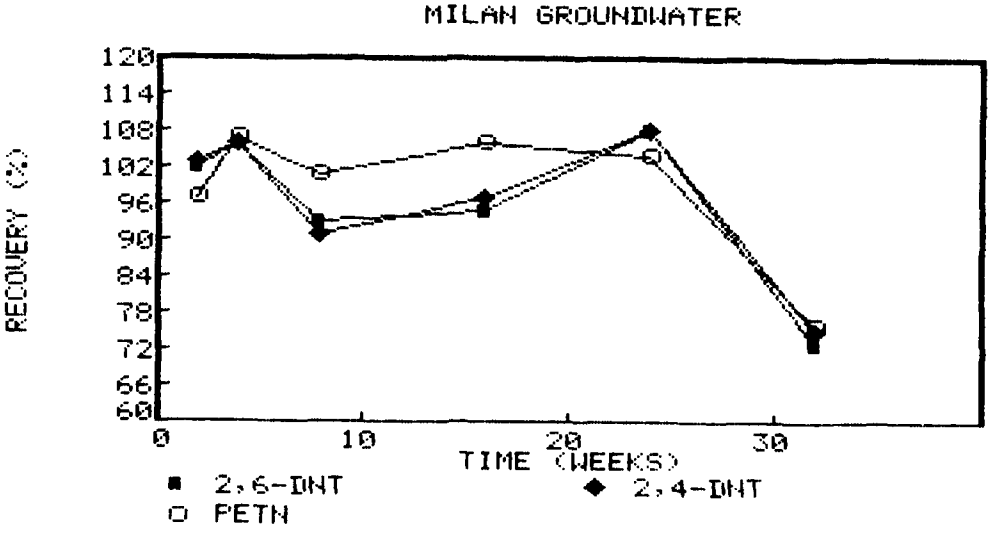
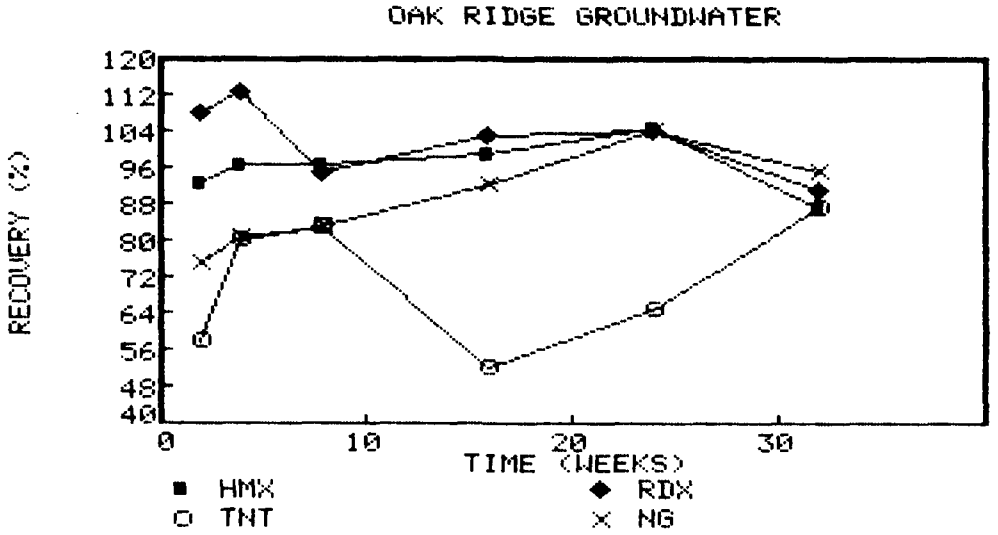


Figure 12. Stability of Explosives Adsorbed on Porapak-R. Source Water: Milan Groundwater



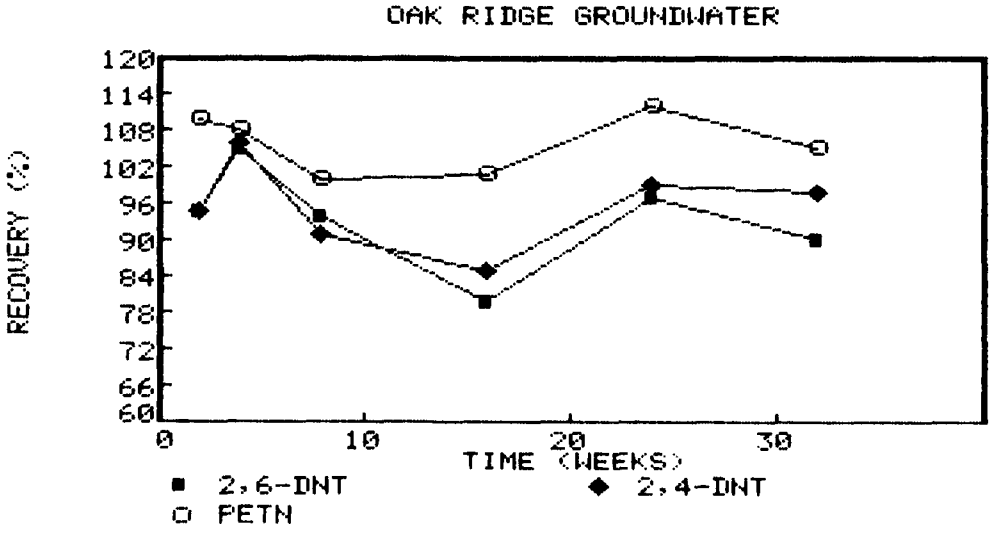
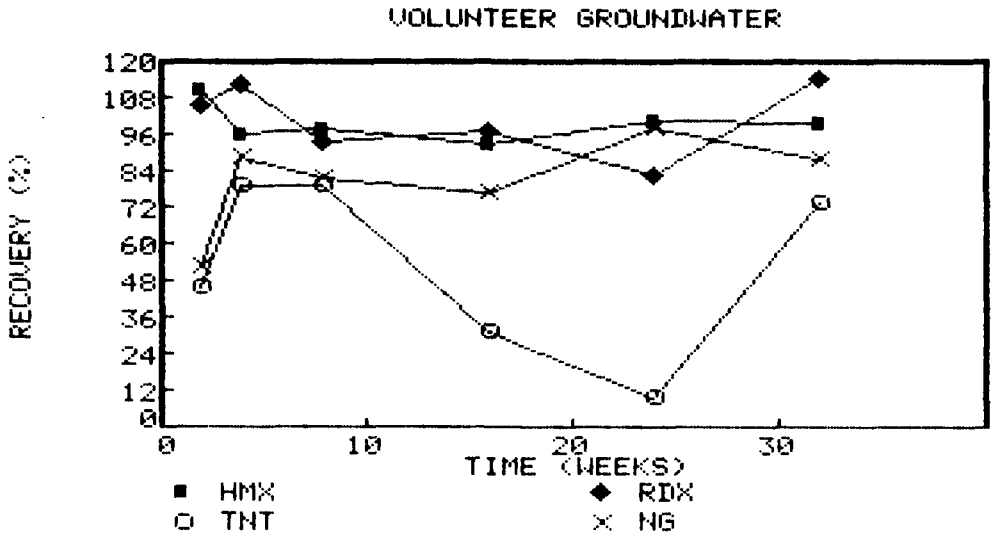


Figure 13. Stability of Explosives Adsorbed on Porapak-R. Source Water: Oak Ridge Ground Water



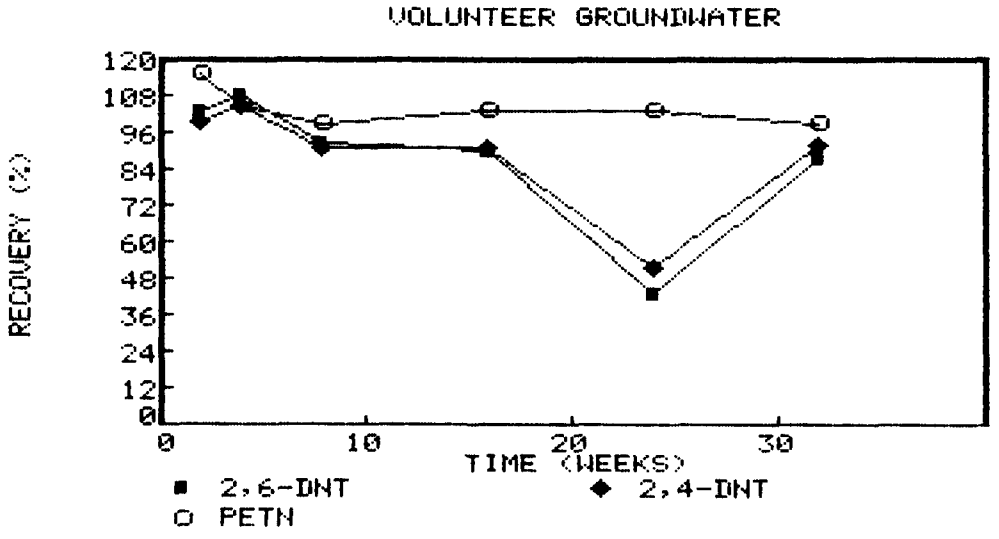


Figure 14. Stability of Explosives Adsorbed on Porapak-R. Source Water: Volunteer Groundwater

does appear that the useful storage time for the resin-adsorbed samples is at least 16 weeks, and is probably much longer for most components.

CONCLUSIONS

The following conclusions can be drawn based on the data generated in this work.

- HPLC with electrochemical detection provides a versatile, sensitive means of determining a wide range of munitions components.
- Resin adsorption on XAD-4, Porapak-R or Porapak-S provides a reliable isolation of HMX, RDX, TNT, 2,6-DNT, and 2,4-DNT over a range of 1 ug/L to 50 mg/L.
- It is likely that NG, PETN, SEX and TAX can also be isolated reliably using the Porapak resins.
- The Porapak resins specifically adsorb the components containing nitro groups regardless of hydrophobicity.
- XAD-4 behaves as a reverse-phase adsorbent, its capacity increasing with the hydrophobicity of the component.
- Using the XAD-4 resin system, many samples can be sorbed in a single day by gravity flow.
- Using the Porapak system, up to eight samples can be collected per day per sampling pump.
- The Porapak-S provides the cleanest background, and is thus best suited for ultra trace analysis.
- The Porapak-R provides the best capacity, and is thus best suited for explosives analysis requiring a wide linear dynamic range.
- TETRYL could not be effectively recovered using either of the Porapak resins. However, XAD-4 is suitable for the quantitative determination of tetryl, at least over the range studied here.

- Nitroguanidine could not be effectively sorbed by any of the resins, but could be analyzed by HPLC-EC.

- All of the explosives are stable on the resin cartridges for at least 16 weeks, and very likely can be stored for much longer periods of time.

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APPENDIX A

PROCEDURE FOR THE COLLECTION OF EXPLOSIVES FROM WATER FOR STORAGE AND ANALYSIS

PROCEDURE FOR THE COLLECTION OF EXPLOSIVES FROM WATER FOR STORAGE AND ANALYSIS WHEN TETRYL IS PRESENT

1. Application

This method is applicable to ground and surface water and is suitable for the preservation of samples for future analysis. The method has been validated for RDX, Tetryl, TNT, 2,6-DNT, and 2,4-DNT.

a. Tested Concentration Range: (ug/L)

RDX: 1-20
Tetryl: 1-20
TNT: 1-20
2,6-DNT: 1-20
2,4-DNT: 1-20

b. Sensitivity: The sensitivity of this method is dependent on the concentration factor. A 500 mL sample concentrated to 5 mL gives a concentration factor of 100, which is applicable to the above concentration range.

c. Detection Limit: (ug/L)

RDX: 2
Tetryl: 2
TNT: 2
2,6-DNT: 2
2,4-DNT: 2

d. Collection Rate: The collection of a 500 mL sample requires approximately four hours. Any number of samples can be extracted simultaneously.

e. Measurement Procedure: Any approved analytical method can be applied to the measurement of the munitions in the collected extract. The data presented here are the result of measurement by HPLC with electrochemical detection at a hanging-mercury-drop (HMDE) working electrode poised at -1.0V vs Ag/AgCl reference electrode.

2. Apparatus

a. Hardware:

1/4" teflon tubing, 2'
1/8" teflon tubing, 3'
1/4 to 1/8 reducing union
1/4 to 1/4 reducing union

b. Glassware:

1/4" borosilicate glass tubes, 10" in length
Soxhlet extractor, 200 mL capacity
Ehrlenmeyer flask, 1 L
Volumetric flask, 500 mL (1/sample)
Centrifuge tubes, 15 mL, screw-capped (1/sample)
Pyrex wool

c. Chemicals:

Methanol, distilled-in-glass grade
Acetone, distilled-in-glass grade
Water, organic-free
RDX
Tetryl
TNT
2,6-DNT
2,4-DNT
XAD-4, 20-60 mesh

3. Standard:

Concentrated stock solutions of RDX, Tetryl, TNT, 200 mg of the SARM material with pure ethyl alcohol to a volume of 100 mL. Solutions were stored at 4°C in the dark using a class II magazine in a flammable materials rated refrigerator.

Stock solution A containing a mixture of TNT, 2,6-DNT, 2,4-DNT at 20 ug/mL was prepared by adding 1 mL each of the concentrated stock solution to 100 mL volumetric flask and diluting the volume with ethanol.

Stock solution B containing a mixture of RDX and tetryl at 20 ug/mL was prepared by adding 1 mL of the concentrated stock solutions to 100 mL volumetric flask and diluting to volume with ethanol.

Solutions for recovery studies at multiples of detection limit (DL) were prepared from the standard solutions as follows:

10 DL: 100 uL of stock solution A and 100 uL of stock solution B to 100 mL water. Calibration standards in 5 mL mobile phase.

5 DL: 50 uL of stock solution A and 50 uL of stock solution B to 100 uL uL water. Calibration standards in 5 mL mobile phase.

2 DL: 50 uL of stock solution A and 50 uL of stock solution B to 250 mL water. Calibration standards in 5 mL mobile phase.

1 DL: 25 uL of stock solution A and 25 uL of stock solution B to 250 mL water. Calibration standards in 5 mL mobile phase.

0.5 DL: 25 uL of stock solution A and 25 uL of stock solution B to 500 mL water. Calibration standards in 5 mL mobile phase.

4. Procedure:

The XAD-4 resin to be used is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extration, the acetone is drained from the resin and replaced with methanol. After the Soxhlet extraction, the resin is never allowed to dry out. The cleaned resin is stored in an Ehrlynmeyer flask under methanol until the collection cartridges are filled.

The cartridges (1/4" x 10" glass tubes) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and capped union is attached. The tube is filled with methanol and all air bubbles removed. A slurry of XAD-4 in methanol is then added, and the methanol is allowed to drain slowly from the cartridge by loosening the union cap. When sufficient resin has been added to bring the level within 1/4" of the top of the tube, a second glass wool plug is inserted and the ends are capped. The capping can be accomplished using capped unions or, more economically, by submerging the tube in methanol.

For collection of the sample, the tubes are uncapped and 50 mL of organic-free water are passed through the column (gravity flow) in order to remove the methanol. The sample is placed in a volumetric flask of 500 mL volume (smaller volumes can be used if the levels of munitions are expected to be high). Teflon tubing (1/8") is used to siphon the water sample through the resin cartridge by gravity flow. The flow rate should be adjusted to 3-6 mL/min. The entire sample is allowed to drain through the cartridge. Again, the cartridge is not allowed to go dry. Ten mL of organic-free water is added to the tube after the sample has been collected; the tube is capped; and refrigerated at 4°C prior to analysis.

The tubes are desorbed by first passing dry nitrogen (~10 lbs pressure) through the tubes for ten minutes to remove the excess water. The tubes are inverted and the munitions are desorbed by passing acetone through the columns (gravity flow) in the opposite direction as the aqueous sample flow. The first 5 mL are collected for analysis. This acetone extract is the final sample for measurement of the munitions.

Analyze the sample for tetryl as soon as possible. Acetone solutions of tetryl are not stable for extended periods (days).

REPLICATE 1 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
RDX	1	0.34	34
	2	2.40	120
	4	5.30	130
	10	12.0	120
	20	20.4	102
TETRYL	1	1	100
	2	1.52	76
	4	4.80	120
	10	8.90	89
	20	17.60	88
TNT	1	0.77	77
	2	1.44	72
	4	4.76	119
	10	9.80	98
	20	21.0	105
2,6-DNT	1	0.66	66
	2	2.10	106
	4	4.60	115
	10	8.90	89
	20	20.2	101
2,4-DNT	1	0.71	71
	2	1.88	94
	4	3.80	95
	10	8.60	86
	20	17.2	86

REPLICATE 2 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
RDX	1	1.10	110
	2	2.20	110
	4	2.88	72
	10	5.0	50
	20	21.0	105
TETRYL	1	1.20	120
	2	1.60	80
	4	2.52	63
	10	7.10	71
	20	24.0	120
TNT	1	0.58	58
	2	1.64	82
	4	3.48	87
	10	9.20	92
	20	19.0	95
2,6-DNT	1	0.39	39
	2	1.58	79
	4	3.48	87
	10	10.7	107
	20	17.4	87
2,4-DNT	1	0.38	38
	2	1.62	81
	4	3.48	87
	10	10.8	108
	20	17.4	87

REPLICATE 3 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
RDX	1	0.92	92
	2	1.18	59
	4	3.52	88
	10	9.20	92
	20	23.6	118
TETRYL	1	0.50	50
	2	1.00	50
	4	3.00	75
	10	6.20	62
	20	19.0	95
TNT	1	0.49	49
	2	1.48	94
	4	3.28	82
	10	8.90	89
	20	19.2	96
2,6-DNT	1	0.35	35
	2	1.72	86
	4	3.32	83
	10	6.80	68
	20	16.60	83
2,4-DNT	1	0.35	35
	2	1.20	60
	4	3.24	81
	10	5.3	53
	20	15.8	79

REPLICATE 4 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
RDX	1	0.30	30
	2	1.30	65
	4	4.80	120
	10	4.10	41
	20	24.0	128
TETRYL	1	0.30	30
	2	0.90	45
	4	4.12	103
	10	5.00	50
	20	22.0	110
TNT	1	1.02	102
	2	1.78	89
	4	4.12	103
	10	7.90	79
	20	15.8	79
2,6-DNT	1	0.60	60
	2	2.04	102
	4	4.36	109
	10	8.80	88
	20	15.0	75
2,4-DNT	1	0.63	63
	2	1.50	75
	4	4.32	108
	10	8.80	88
	20	17.4	87

PROCEDURE FOR THE COLLECTION OF EXPLOSIVES FROM WATER FOR STORAGE AND ANALYSIS

1. Application

This method is applicable to ground and surface water and is suitable for the preservation of samples for future analysis. The method has been validated for HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT and PETN.

a. Tested Concentration Range: (ug/L)

HMX: 10-200
RDX: 2-40
TNT: 2-40
NG: 10-200
2,6-DNT: 2-40
2,4-DNT: 2-40
PETN: 10-200

b. Sensitivity: The sensitivity of this method is dependent on the concentration factor. A 500 mL sample concentrated to 10 mL gives a concentration factor of 50 which is applicable to the above concentration range.

c. Detection Limit: (ug/L)

HMX: 20
RDX: 4
TNT: 4
NG: 20
2,6-DNT: 4
2,4-DNT: 4
PETN: 20

d. Collection Rate: The collection of a 500 mL sample requires approximately four hours. Any number of samples can be extracted simultaneously.

e. Measurement Procedure: Any approved analytical method can be applied to the measurement of the munitions in the collected extract. The data presented here are the result of measurement by HPLC with electrochemical detection.

2. Apparatus

a. Hardware:

Constant-flow pump capable of 15 mL/min at 30 PSIG.
1/4" teflon tubing, 2'
1/8" teflon tubing, 3'
1/4 to 1/8 reducing union
1/4 to 1/4 reducing union

b. Glassware:

1/4" borosilicate glass tubes, 10" in length
Soxhlet extractor, 200 mL capacity
Ehrlenmeyer flask, 1 L
Volumetric flask, 500 mL (1/sample)
Centrifuge tubes, 15 mL, screw-capped (1/sample)
Pyrex wool

c. Chemicals:

Methanol, distilled-in-glass grade
Acetone, distilled-in-glass grade
Water, organic-free
HMX
RDX
TNT
NG
2,6-DNT
2,4-DNT
PETN
XAD-4, 20-60 mesh

3. Standards:

Concentrated stock solutions of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN were prepared by diluting 100 mg of the SARM material with pure ethyl alcohol to a volume of 100 mL. Solutions were stored at 4°C in the dark using a class II magazine in a flammable materials rated refrigerator. The solution of HMX was diluted to 200 mL using a mixture of ethyl alcohol and ethyl acetate (50/50).

Stock solutions of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN at a concentration of 200 ug/mL were prepared by adding 20 mL of the concentrated HMX stock solution to 10 mL of the other concentrated stock solutions to 100 mL volumetric flasks and diluting with ethyl alcohol.

Solutions for recovery studies at multiples of detection limit (DL) were prepared from the standard solutions as follows: 10 DL: 50 uL of RDX, TNT, 2,6-DNT, 2,4-DNT, and 250 uL HMX and PETN to 250 mL water. Calibration standards in 10 mL mobile phase.

5 DL: 25 uL of RDX, TNT, 2,6-DNT, 2,4-DNT, and 125 uL HMX and PETN to 250 uL water. Calibration standards in 10 mL mobile phase.

2 DL: 20 uL of RDX, TNT, 2,6-DNT, 2,4-DNT, and 100 uL HMX and PETN to 500 mL water. Calibration standards in 10 mL mobile phase.

1 DL: 10 uL of RDX, TNT, 2,6-DNT, 2,4-DNT, and 50 mL HMX and PETN to 500 mL water. Calibration standards in 10 mL mobile phase.

0.5 DL: 10 uL of RDX, TNT, 2,6-DNT, 2,4-DNT, and 50 uL of HMX and PETN to 1 L water. Calibration standards in 10 mL mobile phase.

4. Procedure:

The XAD-4 resin to be used is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extraction, the acetone is drained from the resin and replaced with methanol. After the Soxhlet extration, the resin is never allowed to dry out. The cleaned resin is stored in an Ehrlynmeyer flask under methanol until the collection cartridges are filled.

The cartridges (1/4" x 10" glass tubes) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and capped union is attached. The tube is filled with methanol and all air bubbles removed. A slurry of XAD-4 in methanol is then added, and the methanol is allowed to drain slowly from the cartridge by loosening the union cap. When sufficient resin has been added to bring the level within 1/4" of the top of the tube, a second glass wool plug is inserted and the ends are capped. The capping can be accomplished using capped unions or, more economically, by submerging the tube in methanol.

For collection of the sample, the tubes are uncapped and 25 mL of organic-free water are pumped through the column in order to remove the methanol. The sample is placed in a volumetric flask of 500 mL volume (smaller volumes can be used if the levels of munitions are expected to be high). Teflon tubing

(1/8") is used to siphon the water sample through the resin cartridge by gravity flow. The flow rate should be adjusted to 3-6 mL/min. The entire sample is allowed to drain through the cartridge. Again, the cartridge is not allowed to go dry. Ten mL of organic-free water is added to the tube after the sample has been collected; the tube is capped; and refrigerated at 4°C prior to analysis.

The tubes are first dried by passing dry nitrogen (~10 lbs pressure) through the tubes for ten minutes to remove the excess water. The tubes are desorbed by passing acetone through the columns (gravity flow). The first 10 mL are collected for analysis. This acetone extract is the final sample for measurement of the munitions.

REPLICATE 1 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	10	16	160
	20	33	165
	40	66	165
	100	130	130
	200	240	120
RDX	2	1.7	85
	4	3.9	99
	8	9	112
	20	19	94
	40	32	80
TNT	2	1.4	70
	4	3	75
	8	7	83
	20	20	100
	40	39	97
NG	10	10	100
	20	23	115
	40	30	75
	100	30	30
	200	134	68
2,6-DNT	2	1.3	65
	4	3	75
	8	5	60
	20	18	90
	40	32	80
2,4-DNT	2	1.3	65
	4	3	75
	8	5	62
	20	18	90
	40	34	85
PETN	10	8	80
	20	18	90
	40	33	83
	100	102	102
	200	282	140

REPLICATE 2 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	10	15	150
	20	33	163
	40	49	120
	100	145	145
	200	230	115
RDX	2	1.8	90
	4	4.2	106
	8	7	87
	20	21	105
	40	44	112
TNT	2	1.9	95
	4	3.6	91
	8	8	100
	20	29	145
	40	38	96
NG	10	9	90
	20	24	118
	40	56	140
	100	57	57
	200	200	100
2,6-DNT	2	1.3	70
	4	3	75
	8	5	63
	20	18	93
	40	32	80
2,4-DNT	2	1.7	85
	4	4	100
	8	9	108
	20	20	100
	40	41	106
PETN	10	9.5	95
	20	20.5	102
	40	40	100
	100	104	104
	200	176	88

REPLICATE 3 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	10	16	160
	20	31	157
	40	63	158
	100	142	142
	200	244	122
RDX	2	1.8	90
	4	4.6	115
	8	5	67
	20	12	57
	40	34	84
TNT	2	1	50
	4	3	75
	8	7.6	95
	20	20	100
	40	38	95
NG	10	8.6	86
	20	24	119
	40	39	97
	100	55	55
	200	156	78
2,6-DNT	2	1.5	75
	4	3.7	92
	8	7	83
	20	19	93
	40	34	85
2,4-DNT	2	1	50
	4	3	75
	8	6	75
	20	19	93
	40	34	86
PETN	10	9	90
	20	20	100
	40	38	95
	100	95	95
	200	182	91

REPLICATE 4 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	10	14	140
	20	31	155
	40	76	190
	100	131	131
	200	236	118
RDX	2	1	50
	4	4	105
	8	9	114
	20	19	94
	40	30	73
TNT	2	1.9	95
	4	3	75
	8	7.7	96
	20	16.2	81
	40	37	92
NG	10	6	60
	20	23	115
	40	30	75
	100	97	97
	200	138	69
2,6-DNT	2	1.5	75
	4	3.6	90
	8	5.6	70
	20	19	95
	40	34	85
2,4-DNT	2	1	50
	4	3.5	89
	8	5.5	69
	20	19	95
	40	34	81
PETN	10	9	90
	20	17.4	87
	40	38	95
	100	95	95
	200	182	91

PROCEDURE FOR THE COLLECTION OF EXPLOSIVES FROM WATER
FOR STORATE ANALYSIS

1. Application

This method is applicable to ground and surface water and is suitable for the preservation of samples for future analysis. The method has been validated for HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN.

a. Tested Concentration Range: (ug/L)

HMX: 2-40
RDX: 0.5-10
TNT: 0.5-10
NG: 1-20
2,6-DNT: 0.5-10
2,4-DNT: 0.5-10
PETN: 1.5-30

b. Sensitivity: The sensitivity of this ethod is dependent on the concentration factor. A 500 mL sample concentrated to 20 mL gives a concentration factor of 250. Thus, the sensitivity is 250 times lower than that of the analytical method.

c. Detection Limit: (ug/L)

HMX: 4
RDX: 1
TNT: 1
NG: 2
2,6-DNT: 1
2,4-DNT: 1
PETN: 3

d. Collection Rate: The collection of a 500 mL sample requires approximately 30 min. Any number of samples can be extracted simultaneously.

e. Measurement Procedure: Any approved analytical method can be applied to the measurement of the munitions in the collected extract. The data presented here are the result of measurement by HPLC with electrochemical detection.

2. Apparatus

a. Hardware:

Constant-flow pump capable of 40 mL/min at 30 PSIG.
1/4" teflon tubing, 2'
1/8" teflon tubing, 3'
Union: 316 SS 1/4" tube to 3/8" female NPT
Nipple: 316 SS 3/8" NPT x 6"
1/4" SS caps

b. Glassware:

50 mL graduated cylinder
Soxhlet extractor, 200 mL capacity
Ehrlenmeyer flask, 1 L
Volumetric flask, 500 mL (1/sample)
Pyrex wool

c. Chemicals:

Methanol, distilled-in-glass grade
Acetone, distilled-in-glass grade
Water, organic-free
HMX
RDX
TNT
NG
2,6-DNT
2,4-DNT
PETN
Porapak-R, 100-120 mesh

3. Standards:

Concentrated stock solutions of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN were prepared by diluting 100 mg of the SARM material with pure ethyl alcohol to a volume of 100 mL. Solutions were stored at 4°C in the dark using a class II magazine in a flammable materials rated refrigerator. The solution of HMX was diluted to 200 mL using a mixture of ethyl alcohol and ethyl acetate (50/50).

Stock solutions of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT, and PETN at a concentration of 200 ug/mL were prepared by adding 20 mL of the concentrated HMX stock solution to 10 mL of the other concentrated stock solutions to 100 mL volumetric flasks and diluting with ethyl alcohol.

Stock solution mixtures of TNT, 2,6-DNT, 2,4-DNT at 2 ug/mL each munition were prepared by adding 1 mL TNT (200 ug/mL), 1 mL of 2,6 DNT (200 ug/mL), and 1 mL of 2,4-DNT (200 jg/mL) to 100 mL vol flask and diluting to volume with ethanol. Standard mixture A.

Stock solution mixtures of HMX (80 ug/mL), RDX (20 ug/mL), nitroglycerine (40 ug/mL) and PETN (60 ug/mL) were prepared by adding 8 mL of HMX (1 mg/mL) and 3 mL PETN (2 mg/mL) to 100 mL vol flask and diluting to volume with ethanol. Standard mixture B.

Solutions for recovery studies at multiples of detection limit (DL) were prepared from the standard solutions as follows:

10 DL: 1.25 mL of standard mixture A and 125 uL of standard mixture B to 250 mL water. Calibration standards in 2 mL mobile phase.

5 DL: 0.625 mL mixture A and 60 uL of mixture B to 250 uL water. Calibration standards in 2 mL mobile phase.

2 DL: 0.5 mL mixture A and 50 uL of mixture B to 500 mL water. Calibration standards in 2 mL mobile phase.

1 DL: 0.250 mL mixture A and 25 uL mixture B to 500 mL water. Calibration standards in 2 mL mobile phase.

0.5 DL: 0.250 mL mixture A and 25 uL mixture B to 1 L water. Calibration standards in 2 mL mobile phase.

4. Procedure:

The Porapak-R resin is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extraction, the acetone is drained from the resin and replaced with methanol. After the Soxhlet extraction, the resin is never allowed to dry out. The cleaned resin is stored in an Ehrlynmeyer flask under methanol until the collection cartridges are filled.

The cartridges (3/8" x 6" 316 S.S. pipe) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and a capped union is attached. The tube is filled with methanol and all air bubbles removed. A slurry of Porapak-R in methanol is then added, and the methanol is allowed to drain slowly from the cartridge by loosening the union cap. When

sufficient resin has been added to bring the level within 1/2" of the top of the tube, a second glass wool plug is inserted and the ends are capped. The capping can be accomplished using capped 316 SS 3/8" NPT x 1/4" tube unions.

For collection of the sample, the tubes are uncapped and 100 mL of organic-free water are pumped through the column in order to remove the methanol. The sample is placed in a volumetric flask of 500 mL volume (smaller volumes can be used if the levels of munitions are expected to be high). Teflon tubing (1/4") is used to pump the water sample through the resin cartridge using a constant-flow pump. The flow rate should be adjusted to 10-15 mL/min. The entire sample is passed through the cartridge. Again, the cartridge is not allowed to go dry. Twenty mL of organic-free water is added to the tube after the sample has been collected; the tube is capped; and refrigerated at 4°C prior to analysis.

Subsequently, the excess water is removed by passing dry nitrogen through the column for approximately 20 minutes at about 10 psi gauge pressure. The tubes are then desorbed by passing acetone through the tube at a rate of 3 mL/min by gravity flow. Three to five drops of acetone are allowed to drain from the tube, and the next 30 mL are collected for analysis. This acetone extract is concentrated under N_2 to a final volume of 2 mL for analysis.

REPLICATE 1 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	2	1.8	90
	4	4.4	110
	8	10.4	130
	20	20.2	101
	40	52	130
RDX	0.5	0.50	100
	1	0.82	82
	2	2.0	100
	5	4.8	96
	10	11.3	113
TNT	0.5	0.4	82
	1	0.49	49
	2	0.98	49
	5	3.5	70
	10	8.5	85
NG	1	0.62	62
	2	1.3	65
	4	2.2	56
	10	5.4	54
	20	14.4	72
2,6-DNT	0.5	0.25	50
	1	0.39	39
	2	1.2	60
	5	2.3	45
	10	1.9	19
2,4-DNT	0.5	0.25	50
	1	0.28	28
	2	1.5	75
	5	1.3	26
	10	5.0	50
PETN	1.5	0.64	43
	3	1.6	54
	6	4.5	80
	15	12.5	83
	30	25.8	86

REPLICATE 2 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	2	1.1	55
	4	6.0	150
	8	8.2	103
	20	19.2	96
	40	32.4	81
RDX	0.5	0.35	70
	1	0.81	81
	2	1.9	93
	5	4.8	95
	10	11.4	114
TNT	0.5	0.24	48
	1	0.50	50
	2	1.4	72
	5	4.4	87
	10	10.6	106
NG	1	0.62	62
	2	1.3	66
	4	1.4	34
	10	8.5	85
	20	20.6	103
2,6-DNT	0.5	0.26	52
	1	0.78	78
	2	1.6	82
	5	2.5	50
	10	5.0	50
2,4-DNT	0.5	0.25	50
	1	0.57	57
	2	1.7	83
	5	3.7	74
	10	6.6	66
PETN	1.5	0.75	50
	3	2.1	69
	6	5.5	91
	15	12.8	85
	30	39.0	130

REPLICATE 3 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	2	0.6	30
	4	5.8	147
	8	10.4	130
	20	26.0	130
	40	34.4	86
RDX	0.5	0.50	100
	1	0.72	72
	2	2.0	100
	5	4.6	91
	10	12.0	120
TNT	0.5	0.26	52
	1	0.29	29
	2	0.70	35
	5	3.3	66
	10	7.0	70
NG	1	0.48	48
	2	0.76	38
	4	1.6	39
	10	5.5	55
	20	14.8	74
2,6-DNT	0.5	0.20	40
	1	0.37	37
	2	1.6	78
	5	3.8	76
	10	7.2	72
2,4-DNT	0.5	0.38	76
	1	0.41	41
	2	1.7	87
	5	4.1	82
	10	9.4	94
PETN	1.5	0.9	60
	3	1.4	46
	6	5.4	90
	15	13.8	92
	30	33.0	115

REPLICATE 4 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
HMX	2	1.5	75
	4	4.4	110
	8	8.5	106
	20	14.8	74
	40	28.8	72
RDX	0.5	0.55	110
	1	1.2	118
	2	1.8	89
	5	4.6	92
	10	10.2	102
TNT	0.5	0.35	60
	1	0.61	61
	2	1.3	67
	5	4.2	84
	10	7.2	72
NG	1	0.60	60
	2	1.6	80
	4	3.0	75
	10	7.7	77
	20	12.0	60
2,6-DNT	0.5	0.45	90
	1	0.78	78
	2	1.5	76
	5	2.5	49
	10	8.2	82
2,4-DNT	0.5	0.40	80
	1	0.58	88
	2	1.8	89
	5	3.7	74
	10	8.6	86
PETN	1.5	1.1	75
	3	2.0	85
	6	5.0	83
	15	14.8	99
	30	21.9	73

PROCEDURE FOR THE DETERMINATION OF NITROGUANIDINE IN AQUEOUS SOLUTION

1. Application

This method is applicable to ground and surface waters. The method has been validated for nitroguanidine.

a. Tested Concentration Range: (ug/L)

Nitroguanidine: 20-400

b. Sensitivity: The sensitivity of this method depends on the concentration factor. A concentration factor of 25 (259 mL to 10 mL) is applicable to the above concentration range.

c. Detection Limit: (ug/L)

Nitroguanidine: 40

d. Volume Reduction Rate: The reduction of 250 mL aqueous sample to 10 mL requires approximately 3 hours. Samples can be processed simultaneously.

e. Measurement Procedure: Any approved analytical method can be applied to the measurement of nitroguanidine in the collected sample. The data presented here are the result of measurement by HPLC with electrochemical detection at a hanging-mercury-drop (HMDE) working electrode poised at -1.2 V vs Ag/AgCl reference electrode.

2. Apparatus

a. Hardware:

Rotary Evaporator, Rotavapor-R, distributed by Scientific Products, Division of American Hospital Supply Corp., McGraw Park, IL 60085,or equivalent.

b. Glassware:

300 mL Rotary Evaporator Flasks, Volumetric Fasks, 250, 100, 10 mL.

c. Chemicals:

Ethanol-distilled in glass grade, Water, organic free, nitroguanidine.

3. Standards:

Concentrated stock solutions of nitroguanidine were prepared by dissolving 200 mg of nitroguanidine* in 100 mL ethanol.

Prepare stock solution A containing 200 mg/mL by diluting 10 mL of the concentrated stock solution to 100 mL with ethanol.

Solutions for recovery studies at multiples of detection limit (DL) were prepared from the standard solutions as follows:

10 DL: 200 uL of stock solution A to 100 mL water. Calibration standards in 10 mL mobile phase.

5 DL: 100 uL of stock solution A to 100 mL water. Calibration standards in 10 mL mobile phase.

2 DL: 100 uL of stock solution A to 250 mL water. Calibration standards in 10 mL mobile phase.

1 DL: 50 uL of stock solution A to 250 mL water. Calibration standards in 10 mL mobile phase.

0.5 DL: 25 uL of stock solution A to 250 mL water. Calibration standards in 10 mL mobile phase.

4. Procedure:

Adjust the water bath of the rotary evaporator to 50°C. Add the aqueous sample to a 300 mL flask and attach to the rotary evaporator. If the sample is turbid, first filter through Whatman #40 filter paper or equivalent. Turn on the cooling water and the asperator vacuum to the rotary evaporator and then adjust the flask rotation control to slow. Reduce the volume of the aqueous solution to < 10 mL (5-8 mL), transfer this solution to 10 mL volumetric flask and dilute to volume with mobile phase. This is the final volume for analysis. Filter a portion of this solution through 4 micron nylon membrane filters before injection onto the LC column.

Preferred samples for this procedure would be aqueous samples that had been passed through Porapak-R adsorbant for munitions collection. Nitroguanidine is not adsorbed by Porapak-R.

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*Nitroguanidine with 20% H_2O; FLUKA AG, Chemische Fabrik CH-9470 Buchs.

REPLICATE 1 DATA

COMPOUND	ADDED (UG/L)	FOUND (UG/L)	RECOVERY (%)
Nitro-guanidine	20	9	47
	40	25	63
	80	68	85
	200	166	83
	400	412	103
		REPLICATE 2 DATA	
	20	11	53
	40	25	62
	80	86	108
	200	138	69
	400	448	112
		REPLICATE 3 DATA	
	20	13	66
	40	20	50
	80	76	95
	200	140	70
	400	328	82
		REPLICATE 4 DATA	
	20	12	60
	40	19	48
	80	70	87
	200	240	120
	400	384	96

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